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Relation of Charge to Frictional Work in the Static Electrification of Filaments

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Abstract

A study of the generation of electrical charge on fibrous materials was carried out using the apparatus of Hersh and Montgomery, in which a fiber is held fixed in an insulated lower yoke while a second fiber in a grounded upper yoke is rubbed across it under controlled ambient and mechanical conditions. The original apparatus was modified to permit measurement of the frictional work of rubbing as well as the charge. Precautions were taken to discharge both fibers with a radioactive source after each measurement.

It was found that, at any one velocity, several thousand rubs were required before steady values of charge transferred and frictional work of rubbing were obtained.

It was also found that the velocity of rubbing affected strongly both the charge transferred and the frictional work of rubbing, the former being found to decrease and the latter to increase with increasing velocity. This has been explained in terms of local heating, plastic junctions, and material transfer which occur during rubbing. An empirical relationship relating the velocity of rub, the frictional work of rubbing, and the charge transferred was found to hold in the great majority of the cases examined.

From the experimental data obtained it was possible to calculate the mechanical energy expended in any one rub and to estimate the resulting electrical energy. Thus for any pair of fibers under a given set of conditions it was possible to calculate the efficiency of the process of converting mechanical energy to triboelectrical energy. At 30° C. and 33% RH, measured efficiencies were very low (0.00–0.42%); at a very low humidity, efficiencies as high as 2.0% were found.

The presence of a lubricant on the fiber surfaces during rubbing was found in most cases to cause a decrease in both the charge and frictional work of rubbing.

Introduction

Extensive work has been reported on the charges produced by the contact of solids, the impact of solids, and the rubbing of solids in the form of large sheet or rod specimens [57, 58, 66, 67, 68, 69, 70, 71, 72, 73, 74]. Work has also been done on the charging of solids by contact alone in the absence of

[1] This paper is based on a part of the dissertation submitted by J. B. Levy in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Princeton University.

rubbing [8, 25, 29, 35], by allowing specimens to slide on inclined planes [7, 18], and by rolling specimens on an inclined plane [55]. In recent years several investigators have studied the static electrification of textile materials and polymer films, using a variety of methods ranging from different ways of passing yarns or fabrics over insulators or metals [2, 20, 21, 23, 27, 30, 47, 50, 56] to the generation and measurement of charge on bundles of fibers and slivers [39, 47]. Studies have also been conducted on solids in the form of dusts or powders and measurements obtained of the charges formed on them when poured or blown into a cloud [10, 11, 13, 14, 17, 42, 60, 62, 63, 67, 78].

It has been pointed out by Arthur [1] that careful experimentation is necessary to obtain reproducible results capable of unambiguous interpretation. In experiments carried out on large samples in the form of sheets or rods, variations can arise due to oxide, moisture or grease films, adsorbed gases, or changes in the surface of the sample arising from repeated rubbing. In cases where the samples are rubbed manually, such factors as the duration, length, and velocity of rub, the normal force between surfaces, or the temperature and relative humidity cannot be exactly controlled or reproduced, making quantitative explanation difficult. When two surfaces are rubbed together there is a maximum charge determined by the gaseous discharge through the surrounding atmosphere. In an effort to obtain results of quantitative significance, Hersh and Montgomery [32] developed an apparatus to rub together single fibers, or bundles of fibers, under controlled conditions such that the charge developed was less than this maximum value.

Several previous investigations were concerned with the establishment of a triboelectric series, defined as a list of substances so arranged that any one of them will become positively charged when it is rubbed against any one of the substances listed below it in the series. These investigations have been carried out over a period of years ranging from 1758 to the present, the earliest listed [6] being those of Wilcke in 1758, Herbert in 1788, and Young in 1807, with several others found in the literature [2, 12, 23, 32, 37, 43, 61, 65]. There is, however, little agreement among the several series, undoubtedly caused by the fact that different experimental techniques and often different materials, or similar materials from different sources, were used. In one case [72], the authors showed that certain materials could be arranged in a circular fashion; that is, if one material is positive to a second which in turn is positive to a third, then the first might be negative to the third, rather than positive as would be expected in a linear arrangement. Thus it can be seen that a triboelectric series is sometimes not even consistent within itself, apart from being in disagreement with series obtained by other workers. By using well defined materials and conditions of rub, however, Hersh and Montgomery [32] were able to prepare a consistent triboelectric series comprising 15 natural and synthetic textile materials.

The experimental work of Hersh and Montgomery [32] is characterized by good reproducibility with respect to measured values of charge generated; i.e., ±5% for a given pair of fibers. They found that the charge depended upon the orientation of the axes of the filaments with respect to the direction of their relative motion. They adopted a symmetrical arrangement in which fibers were mounted at 45° and −45° with respect to the direction of motion in the horizontal plane so that each fiber swept over the same length of the other.

In a more recent paper, Hersh and Montgomery [33] have discussed their experimental results in terms of a theoretical model based on the band structure of the solid state. Further theoretical treatment based on this model has been given by Van Ostenburg and Montgomery [76]. Levy and Dillon [44], using the Hersh-Montgomery apparatus with certain modifications, gave preliminary results at variance with one of the conclusions of Hersh and Montgomery [32]; i.e., under certain conditions the charge developed by rubbing insulator on insulator increased with increasing velocity. Levy and Dillon [44] also reported that, in some cases, part of the triboelectric charge on a fiber appeared to reside

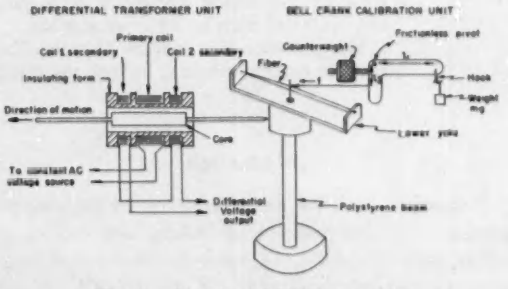

Fig. 1. Sketch of LVDT assembly.

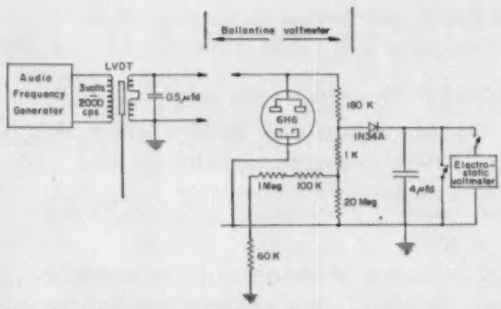

Fig. 2. Diagram of electrical circuit for measuring the integrated frictional force of rubbing.

within the volume of the fiber, since it could not be removed by exposure to alpha particles alone; in fact, penetrating gamma or beta radiations were necessary for complete discharge.

The primary object of the work herein reported was to study the relationship between the static charge and frictional energy of rubbing. It was found necessary, however, to re-examine some of the findings of Hersh and Montgomery in the light of necessary changes in their apparatus and technique.

Apparatus

Rubbing Mechanism and Frictional Work Measurement

The apparatus used in this work was basically that described by Hersh and Montgomery [32], with certain modifications. Essentially the action of this apparatus provides for the rubbing of a fiber held in a grounded upper yoke against another fiber held in a fixed insulated lower yoke, under carefully controlled conditions. Some of the parameters which can be varied using this apparatus are (1) nature of materials, (2) length of stroke, (3) velocity of stroke, (4) tension of fibers, (5) direction of rubbing, (6) normal force, (7) conditions of fiber surfaces, (8) humidity, and (9) temperature. The entire apparatus, except for the motor, cams, and electrometer, is mounted on a grounded copper plate and surrounded by a Faraday cage. The electrical lead from the lower yoke to the electrometer is passed through a grounded brass tube which completely shields the high terminal of the electrometer.

The apparatus was modified in order to measure the energy expended during each rub. The polystyrene insulator serving as the support for the lower yoke was cut into the shape of a rectangular parallelepiped—4.1 cm. × 1.26 cm. × 0.32 cm. A Linear Variable Differential Transformer [2] (hereafter referred to as LVDT) assembly was placed next to this beam. The core of the transformer was mounted on a free-swinging arm, one end of which just touches the top of the polystyrene stand-off insulator (Figure 1). The LVDT is an electromechanical transducer which produces a constant frequency a.c. electrical voltage proportional to the displacement of the movable core. The rectified voltage of the transformer charges a condenser. During a rub, the friction between the two fibers causes the polystyrene beam to deflect and/or oscillate owing to intermittent "stick-slip" motion. The core of the LVDT is displaced from its null position by the deflection of the beam, and the charge on the condenser represents the time integral of all deflections of the beam. This time integral is read as a voltage on an electrometer, providing a measure of integrated frictional force proportional to the mechanical energy of rubbing. At the end of the rub, as soon as the two fibers are separated, the beam returns to its original position, allowing the free-swinging arm to return the core of the transformer to its null position. This process is repeated on each subsequent rub.

The diagram of the electrical circuit for measuring the integrated frictional force is shown in Figure 2. A 3-volt, 2000-cps signal from a Hewlett Packard Audio Frequency Generator, Model 200 A B, is placed across the primary of the Schaevitz transformer, LVDT model 040M-L. The signal from the secondaries of this transformer is amplified through a Ballantine A C Electronic Voltmeter, Model 300A, whose output circuit from the 6H6 stage has been modified as shown in Figure 2. The a.c. output of the Ballantine voltmeter, used as an amplifier, is rectified by a General Electric germanium diode, Type 1N34A; the rectified signal charges a 4-μfd condenser across which a Keithley Electrostatic Voltmeter, Model 29, measures the potential. This potential is proportional to the integrated frictional force of rubbing.

In all other respects but one, the rubbing mechanism was exactly the same as that used by Hersh and Montgomery [32], the exception being that in the present work the normal force was always controlled by the direct method, that is, by positioning the counter-weight on the arm supporting the upper yoke.

[2] Made by Schaevitz Engineering, Camden, N. J.; Type 040M-L.

Test Chamber

Experimental work started in the test chamber developed by Hersh and Montgomery [32]. However, in preliminary experiments involving the rubbing of acetate on nylon, polyethylene on acetate, nylon on acetate, and acetate on polyethylene, the electrical charge was found to vary periodically with the number of rubs. Time variations of temperature, due to the intermittent lighting of the 150-watt incandescent lamp used as a heater, were measured in the humidity chamber and were also found to be periodic, with a range in temperature of approximately 1° C. It was believed that this sinusoidal fluctuation of electrical charge was not a direct effect of ambient temperature on the quantity of charge transferred, but rather an indirect effect of the change of relative humidity with temperature. The humidity in the chamber was kept constant by using saturated salt solutions which gave the required humidity at constant temperature. Fluctuations in temperature, however, caused local changes of the equilibrium between the saturated solution and its vapor and therefore local changes in relative humidity, to which the amount of charge generated triboelectrically is very sensitive.

To correct this condition, an inner chamber made of Celotex [3] and Lucite,[4] in size slightly greater than the Faraday cage [32], was built within the outer plywood and Lucite chamber. This gave a sufficient thermal lag between the outer and inner chambers to make the temperature variation within the inner chamber much less than 1° C. Results obtained with the apparatus after the installation of the inner box showed no trace of the sinusoidal variation of charge due to temperature fluctuations in the outer chamber.

As the second modification, two holes, each 16 mm. in diameter, were bored through the fronts of both chambers, the holes in the front of the outer chamber being protected by two small Lucite sliding doors. The purpose of these holes was to allow an Ionotron [5] radioactive source to be introduced into the inner chamber in two positions, just above the lower fiber and just below the upper fiber, in order to discharge both fibers between rubs. The reason for preferring this method to that used by Hersh and Montgomery [32] will be discussed in a later section.

[3] Trade name for commercial insulating board.
[4] Trade name for polymethyl methacrylate.
[5] Trade name for a radium impregnated foil with appropriate mounting.

Electrical Circuit for Charge Measurements

No changes were made in the electrical circuit of the Hersh-Montgomery apparatus.

Calibration of Frictional Work of Rubbing Measurements

For purposes of comparison, it was decided to calibrate the LVDT device, so as to have a measure of the integrated frictional force (or mechanical work done in rubbing two fibers, one on the other) in units of energy.

This was accomplished with a bell-crank attachment, shown in Figure 1. The horizontal force f applied at the center of the fiber in the lower yoke was known in terms of the weight mg and the arms l_1 and l_2 of the bell-crank; vertical motion h of the weight was measured with a cathetometer. An accurately linear relationship between the force $f\ (=mgl_1/l_2)$ and the motion h was found, indicating that the beam was perfectly elastic in the range of bending strains employed.

Next, a 1-g. weight was hung from the hook on the bell-crank, and the rate at which the condenser was charged by the rectified a.c. voltage of the LVDT was measured by taking electrometer readings at several time intervals. This was repeated using a 2-g. weight. A linear curve of electrometer reading versus time resulted for each weight used; doubling the weight doubled the rate of charging of the condenser. Hence,

$$f = k \cdot \frac{dq}{dt}$$

where k is a constant and dq/dt is the rate of charging of the condenser.

The rate of charging of the condenser by the 2-g. weight was found to be 0.7 electrometer units/sec.; from this the constant k was calculated to be 3480 dyne sec./electrometer unit.

The frictional work of rubbing can be defined as

$$W = v \int f\,dt$$

where v is the constant velocity of rubbing. Substituting for f in this expression,

$$W = kv \int_0^T \frac{dq}{dt} \cdot dt = kv \int_0^Q dq = kv \cdot Q$$

where T is the time during which the rubbing fibers are in contact and Q is the electrometer reading obtained for that rub.

Experimental Conditions

Unless specifically noted otherwise, all experiments described in this work were carried out under the conditions given in Table I.

Sample conditioning time refers to the period that samples were allowed to remain in the apparatus, mounted on their respective yokes and under the given ambient conditions, before rubbing was started. Velocity of stroke refers to the velocity of the point of contact of the two fibers along the direction of the lower fiber, not to the velocity of the driving crank. The contact velocity was found by measuring the time during which the two fibers were actually in contact at any one velocity and then dividing the actual length of stroke by this time. The actual length of stroke is the distance moved by the point of contact of the two fibers, and is measured along either of the two fibers.

The relative humidity was maintained at 33% by the use of a saturated solution of magnesium chloride within the outer and inner chambers. In one experiment Drierite was used to provide a very low humidity.

The type of rub used (45°–45°) was that in which the upper fiber is rubbed over the lower fiber, the direction of motion being at 45° to both fibers. It should be noted that, in this type of rub, fresh surface on one fiber is always coming into contact with fresh surface on the other fiber. This type of rub was preferred to the other possible types (e.g., 90°–0° and 0°–90°), as it was desired to have symmetrical conditions and no preferential heating of either fiber. The charge transferred was always measured on the lower fiber, and the charge transferred to the upper grounded fiber was assumed to be equal in magnitude and opposite in sign.

Experimental Results

Samples

The materials used in the experiments were all in monofilament form except for two of the samples mentioned below. The majority of the experiments involved the use of specially prepared monofilaments of nylon, polyethylene, viscose, cellulose acetate, cellulose triacetate, and Teflon, all of approximately 0.025-cm. diameter. These monofilaments were spun without lubricating or spinning oils, to provide the cleanest possible fiber surfaces. The viscose and cellulose acetate used in some of the earlier experiments were multifilaments of approximately 300 den., prepared commercially. Similarly, the nylon used in early experiments was a commercially prepared monofilament of 0.020-cm. diameter.

TABLE I. Experimental Conditions

Sample conditioning time	15 hr.
Temperature	30° C.
Relative humidity	33%
Type of rub used	45°–45°
Normal force	22.0 g.
Actual length of stroke	2.50 cm.
Tension in each fiber	50.0 g.
Velocity of stroke (low)	0.88 cm./sec.
Velocity of stroke (medium)	1.89 cm./sec.
Velocity of stroke (high)	4.03 cm./sec.
Strokes/hr. (low)	140
Strokes/hr. (medium)	311
Strokes/hr. (high)	673
Capacitance of system without loading condenser	30.3 $\mu\mu$f
Capacitance of system with loading condenser	178 $\mu\mu$f

Since preliminary experiments with both the commercial and special fibers showed that cleaning with methyl alcohol and diethyl ether did not affect the quantity of charge transferred on rubbing, the fibers used in the experiments described were not cleaned in any way. However, great care was taken while mounting the fibers in their respective yokes to prevent the portions which would be in contact during the rubbing from being touched by the hands.

Reproducibility

Successive rubs. Previous work [32] had shown that the number of strokes required to reach a constant electrometer reading on successive rubs ranged from 2 or 3 for polyethylene on nylon to about 60 or 65 for acetate on nylon. Some experiments carried out by the present authors indicated that many more rubs were required in the majority of the cases before a reading was obtained that would remain constant over a large number of rubs, i.e., a steady value of charge transfer. A thorough examination of this effect was made for each pair of fibers tested. The apparatus was allowed to run at the medium velocity, and readings of charge transfer were taken at intervals. Both fibers were discharged with the Ionotron radioactive source before each rub in which a reading was taken. Examples of this behavior are shown in Figure 3 for viscose on nylon and for nylon

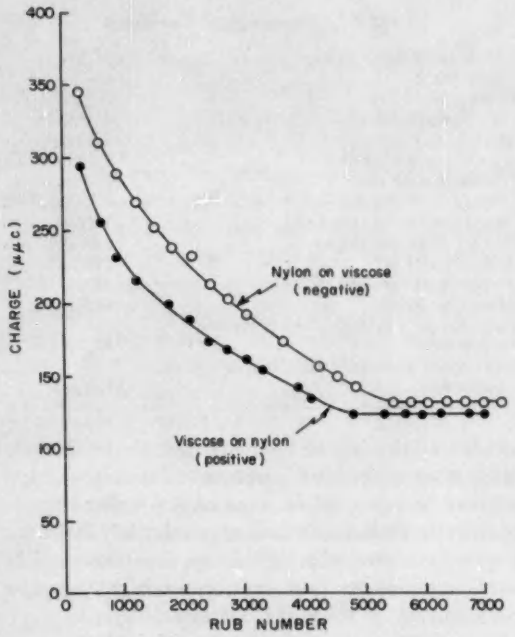

Fig. 3. Charge vs. rub number for nylon on viscose.

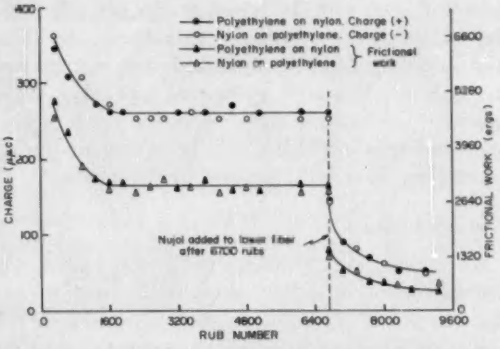

Fig. 4. Effect of rub number and addition of Nujol on charge and frictional work; polyethylene and nylon, medium velocity.

on viscose. It should be noted that the constant values reached in these two cases are opposite in sign, and very nearly equal in magnitude. In all combinations of fibers tried it was found that thousands of strokes were required to reach a steady value of charge transferred.

The charge produced in any one rub is considered to depend on the friction between the two samples, because of the local heating produced by that friction [3]. Therefore, an explanation of why the frictional work decreases with rub number until a reproducible steady value is obtained may also explain why the charge transferred behaves in a similar fashion. Friction between the two fibers is probably caused by interactions of the slant surfaces of asperities present on the surfaces of the two fibers being rubbed. The motion between the two sliding surfaces is thought to be discontinuous, and to proceed by a process of "stick-slip." The "stick" is due to the higher static friction between the surfaces, and the "slip" to the lower kinetic friction during the slip itself. During the "stick" periods, plastic junctions are assumed to be formed by asperities of the two substances being rubbed. These junctions must then be broken as the sliding continues, and it is the material which has the lower resistance to shear that will break at the base of the junction. Thus on repeatedly rubbing the two fibers together, a vast number of such junctions is made and broken, and throughout this rubbing the measured frictional work will continually decrease, since the asperities are being broken off one fiber and not the other. At the point where one fiber remains smooth relative to the other, the frictional work will remain constant. This is the behavior shown in Figures 4–6.

When the same material is rubbed on itself, a different behavior is expected. In this case asperities are not torn off at the base on one of the fibers, since both fibers have the same shear resistance; here it is expected that the plastic junction itself will be the weakest point, and that it will be broken, only to be reformed and rebroken again and again. Thus the frictional work at any one velocity is expected to be independent of rub number, and indeed this was found, as shown in Figures 13 and 14.

Interchanging the fibers. Hersh and Montgomery [32] noted that the positive charge obtained by rubbing polyethylene on nylon was considerably smaller than the negative charge obtained by rubbing nylon on polyethylene; they also observed such differences for several other combinations of materials studied. Since the relative motion of the fibers is the same in the two situations, it is difficult to understand why such biased behavior should occur. When the experimental technique used by Hersh and Montgomery was re-examined, it seemed possible that in the attempt to discharge both fibers by means of the radioactive source, the upper fiber was not completely discharged because of the protection from radiations offered this fiber by the metal protractor

above it. A residual charge on the upper fiber would presumably affect the quantity of charge transferred on the subsequent rub, tending to make it smaller than it would have been had both fibers been completely discharged. This effect would be particularly noticeable in the cases where the fiber in the upper yoke was the better insulator; for example, when polyethylene is rubbed on nylon. The apparatus was therefore modified to permit the complete discharging of both fibers by allowing the radioactive source to be brought to bear directly on both of the fibers. With the modified form of the apparatus, two experiments were carried out: first, polyethylene was rubbed on nylon; second, nylon was rubbed on polyethylene. It was found that the positive charge obtained in the first case was equal in magnitude (within the limits of experimental error) to the negative charge obtained in the second case. The values obtained were:

Polyethylene on nylon: +335 micromicrocoulombs
Nylon on polyethylene: −360 micromicrocoulombs

whereas the averages of the values obtained by Hersh and Montgomery for a number of samples rubbed on several days were:

Polyethylene on nylon: +220 micromicrocoulombs
Nylon on polyethylene: −360 micromicrocoulombs.

It can be seen that there is excellent agreement between the values obtained in the present work and the value obtained for nylon on polyethylene in the previous work. This lends support to the theory suggested above.

Treated human hair.—Some experiments were also carried out on a number of human hair samples, of which sample A was untreated and samples B, C, D, and E had been treated with four commercial shampoos. The object was to learn which of the shampoos gave the most effective lowering of the quantity of charge transferred upon rubbing with respect to the untreated hair. The type of rub chosen for these experiments was that in which the tips of the top fiber move into the roots of the lower fiber. This type of rub had previously been found [32] to give a high positive charge on the lower fiber. In each case hair samples of the same treatment were rubbed on each other, and in two cases duplicate runs were made to check the reproducibility of the results obtained. These results are shown in Figure 7. It can be seen that the reproducibility is very good, and that it is easy to select the treatment given to sample C as the most satisfactory one for reducing static-charge retention of the hair.

Charge and Frictional Work

Effect of rub number and lubricant. Certain experiments mentioned previously indicated that a very large number of rubs was required to reach a truly steady value of charge transferred. Therefore experiments were carried out (a) to investigate the effect of rub number on both the charge transferred and the frictional work of rubbing for different pairs of fibers and (b) to determine the effect on both charge and frictional work of adding a lubricant to the surface of the fibers.

Figure 4 shows the results obtained for nylon on polyethylene and polyethylene on nylon. It can be seen that during the first 2000 rubs both the charge and the frictional work decreased until a value of each was reached which remained constant for the

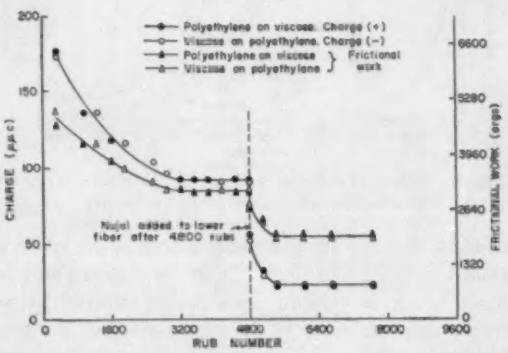

Fig. 5. Effect of rub number and addition of Nujol on charge and frictional work; polyethylene and viscose, medium velocity.

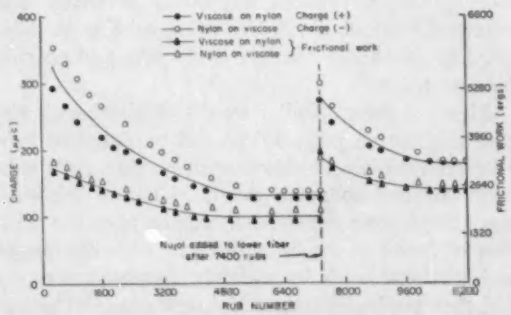

Fig. 6. Effect of rub number and addition of Nujol on charge and frictional work; viscose and nylon, medium velocity.

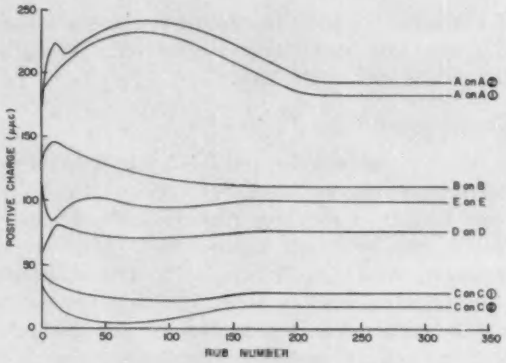

Fig. 7. Charge vs. rub number for untreated human hair on treated and untreated human hair.

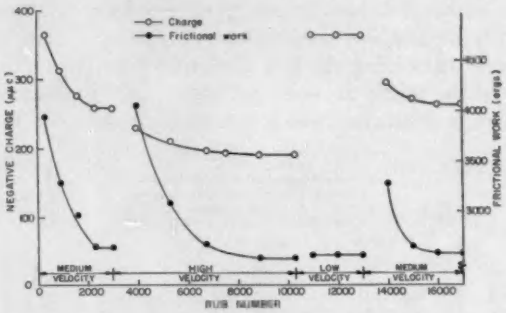

Fig. 8. Effect of velocity and rub number on charge and frictional work; nylon on polyethylene.

next 5000 rubs. At this point a drop of Nujol [6] was placed on the lower fiber. Both the charge and frictional work of rubbing immediately started to decrease and continued to decrease for about the next 1500 rubs, when each again reached new (and lower) steady values which were reproducible over many subsequent rubs. This experiment also shows excellent agreement between the values of charge and frictional work obtained with nylon rubbing on polyethylene and those obtained with polyethylene rubbing on nylon.

Figure 5 shows similar results obtained with viscose rubbing on polyethylene and polyethylene rubbing on viscose. In this case more than 3000 rubs were required to reach steady values of frictional work and charge transferred. Again, upon the addition of Nujol to the fiber surfaces, both the charge and frictional work immediately decreased abruptly and then gradually approached new steady values as rubbing continued.

[6] Trade name for highly refined paraffin oil.

Figure 6 shows the results obtained with nylon on viscose and viscose on nylon. Here more than 5000 rubs were required to reach steady values of the charge and frictional work. In this case, however, the addition of a drop of Nujol to the lower fiber caused both the charge and the frictional work to increase at once and then gradually decrease until new constant values—higher than the original constant values for both parameters—were reached. This was the only case in which the addition of a lubricant caused such an immediate increase; the usual effect was a decrease in both properties.

In hydrodynamic or fluid lubrication, the surfaces in relative motion are separated by a lubricant layer of appreciable thickness and, under "ideal" conditions, there is no wear of the surfaces. The resistance to motion is due predominantly to the viscosity of the interposed layer [34]. In practice, however, it is often impossible to obtain fluid lubrication, particularly if the sliding speeds are low or the loads are high. In such cases the thick lubricant layer breaks down, and the surfaces are separated by lubricant films of only molecular dimensions. Under these conditions, which Hardy referred to as boundary conditions (*cf.* [3]), the friction is influenced by the nature of the underlying surfaces as well as by the chemical nature of the lubricant.

It would be expected, in cases involving fiber systems in which high frictional forces are exhibited, that the addition of lubricant would cause a decrease in the frictional work of rubbing, owing to boundary lubrication action. However, in cases where the frictional work of rubbing two fibers is initially small, it might be expected that the addition of lubricant would have only a slight effect. The increase in the frictional work of rubbing caused by the addition of Nujol to viscose and nylon which had been rubbed many times is an interesting example of the occasionally observed failure of a "lubricant" to lubricate. Obviously, these experiments with Nujol are cursory, and this equipment seems to offer possibilities for more thorough studies of the action of surface coatings on inter-fiber friction.

Effect of velocity. Previous work [32] showed that for insulators rubbed on insulators, no effect of the velocity of rub on the quantity of charge transferred could be found. However, this result may have been due to the fact that comparatively few rubs were used, a condition that might have masked any such effect. Therefore, an experiment was car-

ried out, in which nylon was rubbed on polyethylene at the medium velocity until steady values of charge and frictional work were obtained, to test this possibility. Thereafter, the fibers were rubbed at the low velocity, and finally again at the medium velocity to see if the values obtained with the same velocity at the start would agree with those at the end of the experiment. The results of this experiment are shown in Figure 8. It is seen that different steady values of both charge and frictional work were reached for each rubbing velocity. The steady values reached using the medium rubbing velocity of 1.89 cm./sec., both at the start and at the end of the experiment, are seen to be in close agreement, demonstrating that the observed results were indeed due to an effect of the rubbing velocity rather than to the changes in fiber surfaces brought about by the continued rubbing of one fiber against the other.

A series of such experiments was carried out on a number of different fiber pairs. In every case the same pair was in turn rubbed at low, medium, and high velocity, until constant values of charge and frictional work were reached for each velocity. In every case, the passage from one velocity to a higher velocity after constant values were reached caused a decrease of charge transferred and in most cases an increase in the frictional work of rubbing. Figure 9 shows typical results, plotted as charge vs. square root of frictional work of rubbing. Straight lines result, the slope of each line depending on the pair

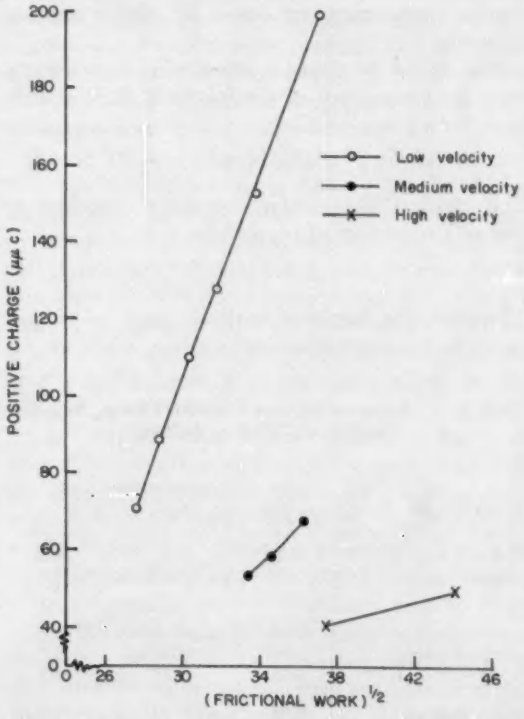

Fig. 9. Charge vs. square root of frictional work at three velocities; cellulose triacetate on nylon.

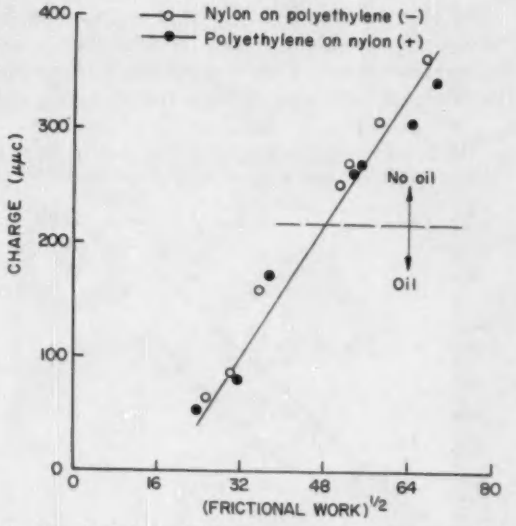

Fig. 10. Effect of Nujol on charge and frictional work; viscose and polyethylene at medium velocity.

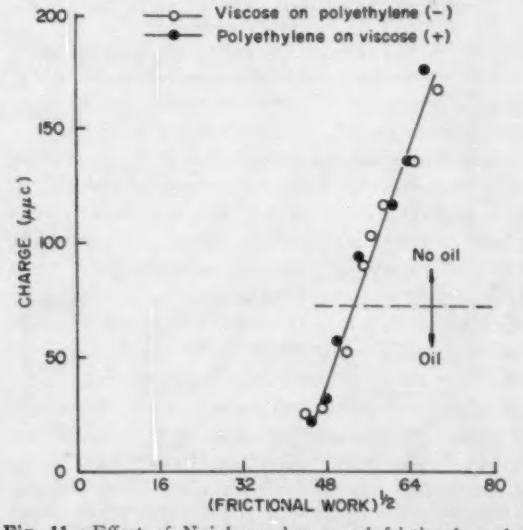

Fig. 11. Effect of Nujol on charge and frictional work; nylon and polyethylene at medium velocity.

of fibers in question and the velocity at which they were rubbed.

Figures 10, 11, and 12 show plots of charge vs. square root of frictional work for viscose and polyethylene, nylon and polyethylene, and viscose and nylon, all rubbed at the medium velocity and showing the effect of lubricant. In every case the slope of the line without lubricant is the same as the slope of the line with lubricant.

The observed decrease in charge and increase in frictional work with increasing velocity may be interpreted as follows. Flow and welding of the plastic junctions are facilitated by high temperatures, and high temperatures result from high rubbing velocities. Therefore, the higher the velocity, the greater are the number of plastic junctions that are formed during a rub, and more work is required to break these junctions. Thus an increase in rubbing velocity should cause an increase in the frictional work of rubbing, in agreement with most of the observations of this work. At a higher velocity of rubbing, however, more asperities would be expected to weld into junctions, and more material transfer would take place from one fiber to the other. If material is transferred from the negatively charged fiber to the positively charged one, the negative charge on the material would neutralize an equal amount of positive charge on the fiber onto which this negatively charged material is transferred, thus causing a decrease in the measured quantity of charge. The higher the velocity, the greater would be the amount of material transferred, thus causing a decrease in the measured quantity of charge. This appears to be a sufficiently dominant factor to offset the effect of exciting a greater number of electrons into the conduction band of the insulator at the higher temperatures produced by higher rubbing velocities.

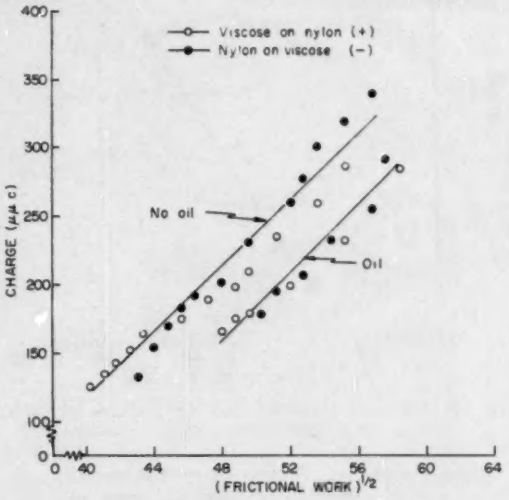

Fig. 12. Effect of Nujol on charge and frictional work; viscose and nylon at medium velocity.

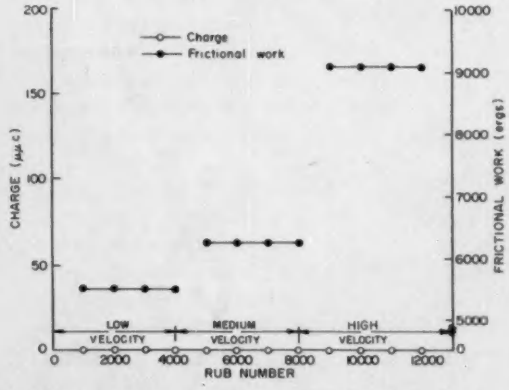

Fig. 13. Effect of velocity and rub number on charge and frictional work at three velocities; polyethylene on polyethylene.

The charge developed is observed to vary linearly with the square root of the frictional work of rubbing, for a given velocity v

$$q = \phi(v) \cdot W^{1/2}$$

The classical formula for the energy required to charge a condenser of capacitance C is

$$E = \tfrac{1}{2}q^2/C$$

Therefore, the frictional work W must be proportional to the electrostatic energy E.

TABLE II. Relations Between Electrical Charge, Rubbing Velocity, and Work of Rubbing

Fiber system	v, cm./sec.	$\frac{dq}{d(W^{1/2})}$, $\mu\mu$ coulombs / erg$^{1/2}$	$\frac{dq}{d(W^{1/2})} \cdot v^{3/2}$
Viscose on nylon	0.88	13.1	10.8
	1.89	4.45	11.5
	4.03	1.20	9.7
Viscose on polyethylene	0.88	18.5	15.3
	1.89	6.67	17.2
	4.03	1.96	15.8
Cell. triacetate on nylon	0.88	12.55	10.4
	1.89	4.86	12.1
	4.03	1.29	10.4

In comparing data for a given pair of fibers at various velocities, however (see Figure 9, for example), it was found that the slope of the curve of q versus $W^{1/2}$ was inversely proportional to the 3/2 power of the velocity v.

$$\frac{dq}{d(W^{1/2})} \cdot v^{3/2} = K$$

No simple physical interpretation of this relationship has yet been developed, but it is given here simply as a possibly useful empirical formula. The data upon which it is based are given in Table II.

Effect of rubbing identical fibers. Figure 13 shows the effect of velocity and rub number on the charge and frictional work for polyethylene rubbed on polyethylene. It can be seen that, as with pairs of different fibers, the frictional work increased with increasing velocity; however, at any one velocity the frictional work remained constant with increasing rub number, in this way differing from the results observed when non-identical fibers were rubbed. The average charge transferred was found to be zero throughout the experiment. However, it should be noted that each point on the graph is the average of a number of experimental readings, and that some of these individual readings showed a small transfer of charge (never more than 2 micromicrocoulombs), sometimes positive and sometimes negative.

Figure 14 shows the results of a similar experiment performed with nylon rubbing nylon. Again the frictional work increased with increasing velocity, but remained constant at any one velocity. The charge remained constant throughout the experiment at a level of about 18 micromicrocoulombs of negative charge transferred to the lower fiber. This result is not understood but could be related to the fact that the fibers were not mounted at exactly 45°–45°, thus biasing the results.

The negligible total charge transfer observed in rubbing one fiber on another of the same type does not necessarily imply that there is no charge transfer at various times during a rub, but rather that the average transfer of charge in an entire rub is zero. Transfers of charge may take place at localized spots along the surfaces of both fibers but, as both fibers are of the same type, these transfers on the average occur in a random manner; at some spots electrons flow from the upper to the lower fiber, at others from the lower to the upper. This concept is supported by photographs taken of the fiber surfaces after repeated rubbing, where it can be seen that small bits of fiber are attached, probably by electrostatic attraction, at points along both fibers (see Figures 17–20).

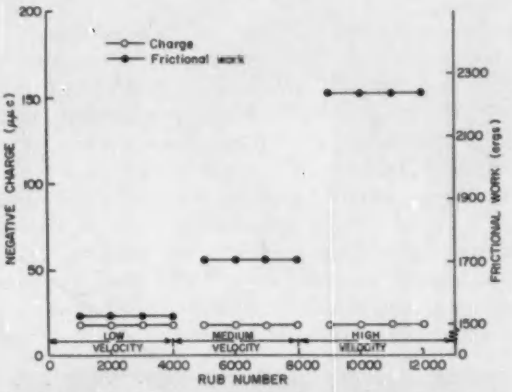

Fig. 14. Effect of velocity and rub number on charge and frictional work at three velocities; nylon on nylon.

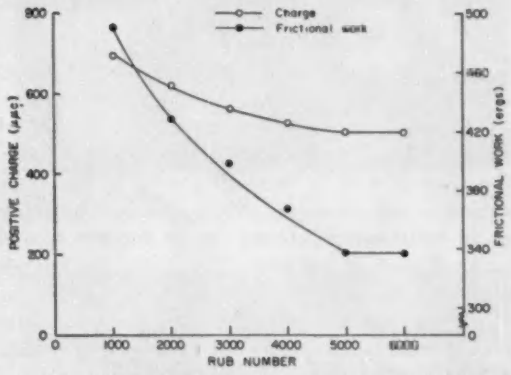

Fig. 15. Effect of rub number on charge and frictional work; cellulose acetate on nylon at ~0% RH.

Effect of very low humidity. An experiment was carried out to find the effect of a low humidity in the ambient atmosphere, rubbing cellulose acetate on nylon. This particular pair of fibers was chosen for the experiment since previous data indicated that a large charge transfer and low frictional work might be expected under these conditions. Fresh samples of these fibers were mounted in a pair of yokes in the apparatus. Trays containing Drierite (anhydrous calcium sulfate) were placed in the apparatus instead of the usual trays containing saturated magnesium chloride solution. After a 48-hr. period of conditioning, to allow equilibrium conditions to be reached in the chamber, rubbing was carried out at the low velocity until steady values of both charge transferred and frictional work of rubbing were ob-

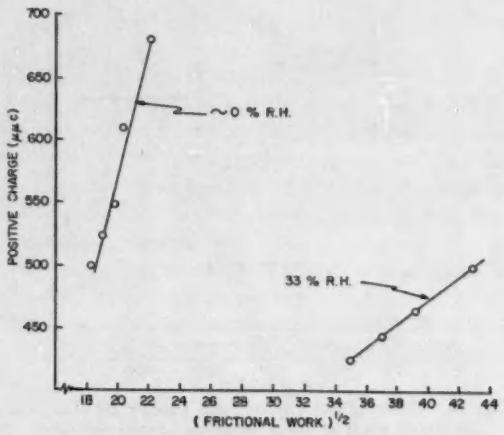

Fig. 16. Charge vs. square root of frictional work; cellulose acetate on nylon, low velocity.

tained. The results are shown in Figure 15 as plots of charge and frictional work vs. rub number; Figure 16 shows a plot of charge vs. square root of frictional work, which again is seen to be linear. The slope is seen to be much greater at the lower humidity, indicating the strong effect of humidity on the relationship between charge transferred and frictional work of rubbing. Decreasing the humidity gave a moderate increase in the charge transferred and a considerable decrease in the frictional work of rubbing, this latter decrease being the more prominent effect.

Efficiency Calculations

The efficiency of the process of converting mechanical energy to triboelectrical energy by means of rubbing two filaments together may be defined as the ratio of the electrical energy which is obtained from the system to the mechanical energy which is introduced into it, i.e.:

$$\text{Efficiency } (\%) = \frac{\text{Electrical energy obtained}}{\text{Mechanical energy provided}} \cdot 100$$

The mechanical energy introduced is simply the frictional work of rubbing. If it is assumed that all the electrical energy obtained from the system is stored in the charged fibers, it is possible to estimate this energy by considering each fiber and yoke system as a condenser. (It can be shown that the energy not in the fibers—e.g., that stored in the loading condenser—is negligible.) The capacitance of such a condenser system can be approximated by using the equation for a condenser in the form of two coaxial cylinders:

$$C = 0.2416\, l/(\log_{10} r_1/r_2)$$

where C is the capacitance in e.s.u., l is the length of charged fiber in cm., r_1 is the distance of the filament above its yoke in cm. (= 1 cm.), and r_2 is the radius of the filament in cm. (= 0.0125 cm.).

By the use of these values, the capacitance C for this system was found to be 0.3 e.s.u. Other condensers of similar geometries (e.g., a wire and an infinite plate, or two parallel wires) give capacitances of the same order of magnitude.

The energy E stored in one fiber is given by the relationship:

$$E = \tfrac{1}{2}q^2/C$$

where q is the charge and C is the capacitance. The total energy stored in both fibers is twice that for a single fiber, and can be calculated for any rub using the values of measured charge and calculated capacitance.

Some examples of efficiency values determined in the manner just described are given in Table III for the experiments at 33% RH and 30° C.

In the belief that higher values of efficiency would be found by working in a drier atmosphere, an experiment (described earlier) was carried out at conditions approximating 0% relative humidity, cellulose acetate being rubbed on nylon at the low velocity. This particular combination of fibers and velocity

TABLE III. Triboelectric Efficiency as a Function of Velocity of Rubbing for Various Fiber Pairs

Fibers rubbed	Velocity	Efficiency, %
Viscose on nylon	low	0.015
	medium	0.010
	high	0.005
Viscose on polyethylene	low	0.025
	medium	0.008
	high	0.003
Cellulose triacetate on nylon	low	0.019
	medium	0.007
	high	0.003
Nylon on polyethylene	low	0.14
	medium	0.072
	high	0.042
Cellulose acetate on nylon	low	0.42
	medium	0.13
	high	0.043

was chosen since it was the one which showed the greatest efficiency at 33% relative humidity. The results of this experiment are shown in Figures 15 and 16. The efficiency of 2.0% was determined from the steady state values of charge and frictional work. For purposes of comparison, the efficiency calculated after 1000 rubs (before the steady values were reached) was also 2.0%. This relatively high efficiency was mainly due to a decrease in the mechanical energy and not to an increase in the electrical energy.

It has been suggested [3] that electrostatic attraction may play a predominant part in the friction between fibers. However, it has been shown that only a very small part of the mechanical energy put into the rubbing of two fibers is converted into electrical energy, and certainly most of the remainder of the mechanical energy is converted into heat (and probably a little into sound also). Thus it would appear that electrostatic attraction, as measured by the triboelectric conversion of energy, does not play a very important role in the friction between fibers. This is in agreement with conclusions reached by Shooter and Tabor for plastic materials [63]. Rather, the friction between fibers appears to be an important factor in producing the static charge.

Fiber Surfaces

Microphotographs were taken of several pairs of fibers after long periods of rubbing. These are shown in Figures 17–22 (magnification 21.5 ×). In each case, the softer fiber is worn down, and small shavings of one fiber are seen to adhere to the other fiber, presumably by electrostatic attraction. There is evidence of material transfer even in cases where identical fibers were rubbed (Figures 21 and 22).

Fig. 17. Triacetate (upper) on nylon (lower) after 14,000 rubs (7000 at low, 4000 at medium, and 3000 at high velocity).

Discussion

Consideration of the results of these experiments reveals several departures from the findings of Hersh and Montgomery [32]. For the most part, these departures can be explained by the different techniques employed, and there is no reason to question the validity of the results obtained under the particular conditions chosen by Hersh and Montgomery for their experiments.

It is not clear how they were able to achieve steady values of charge after only a few rubs, whereas several thousand rubs were found necessary in the present work. Hersh and Montgomery's practice of

Fig. 18. Nylon (upper) on polyethylene (lower) after 17,000 rubs (2700 rubs at low, 6500 at medium, and 7000 at high velocity).

Fig. 19. Viscose (upper) on polyethylene (lower) after 12,000 rubs (4000 at low, medium, and high velocity).

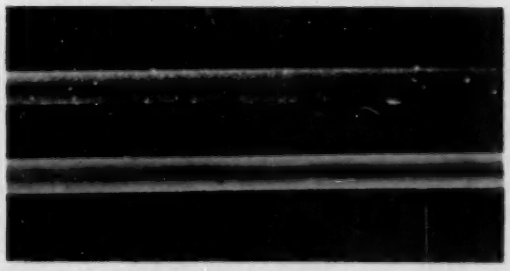

Fig. 20. Acetate (upper) on nylon (lower) after 14,000 rubs (6000 at low, 5000 at medium, and 3000 at high velocity).

Fig. 21. Nylon (upper) on nylon (lower) after 12,000 rubs (4000 rubs at low, medium, and high velocity).

Fig. 22. Polyethylene (upper) on polyethylene (lower) after 12,000 rubs (4000 rubs at low, medium, and high velocity).

discharging the fibers after every charge measurement and before making the next rub apparently does not explain the discrepancy with the current findings, for when their technique was employed by the present authors in several instances, no difference in the results was found. In the present work, therefore, fibers were discharged only before that rub after which the charge was actually measured; the conditioning was achieved by repeated rubbing uninterrupted by discharging.

It is possible, of course, that the type of steady state achieved in the present work was very different from that found by Hersh and Montgomery because of the greater amount of abraded material resulting from long periods of repeated rubbing. This perhaps influenced the charge transfer, as indicated earlier, and also might explain the definite dependence of charge upon velocity of rubbing which was found in this work, contrasted with independence of charge upon velocity generally found by Hersh and Montgomery. The precision obtainable by the techniques employed in the present work is rather gratifying, particularly in that symmetry was achieved in the quantity of charge developed when the fibers were reversed in position from the grounded to the ungrounded yokes and that rubbing like fibers gave negligible charge.

The relationships found between frictional charge and the mechanical work involved in its development appear to be of interest since, to the knowledge of the authors, no experiments yielding both the charge and work in absolute units have been previously reported.[7] Frictional work indeed appears to be an important factor in the development of charge in rubbing; however, much further work will have to be done before the relationship between frictional work and charge is clearly understood. The apparatus and technique do seem to offer possibilities for relating these quantities, and perhaps such experiments might shed new light on the nature of friction.

There would seem to be little point in presenting here a discussion of the results of this work in terms of solid state theory. None of the findings conflicts seriously with recently announced concepts of the transfer of charge due to friction [33, 76]. However, the observation that appreciable amounts of one fiber abrade under the conditions of experiment and cling to the other fiber, thereby surely influencing the net charge transfer, suggests caution in proposing a purely electronic or ionic mechanism of triboelectricity on the basis of experiments of this type.

Acknowledgments

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[7] Quintelier et al. [56] measured coefficient of friction and charge developed for cellulose acetate yarns running over a steel surface and found the charge to increase linearly with coefficient of friction.

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Electrical Forces Affecting Soil and Substrate in the Detergency Process—Zeta Potential

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Abstract

Electrokinetic forces are of considerable importance in the mechanism of soil removal and redeposition. One electrokinetic measurement is that of the difference in potential between the immovable layer attached to the surface of a solid phase (soil or substrate) and the movable part of the diffuse layer in the body of the detergent liquid, and is termed zeta potential. Correlations have been obtained which indicate that, in a detergent system, it is desirable that the zeta potentials of soil particles and substrate become nearly equal to reduce attractive forces tending to cause them to adhere.

The effect of surfactants and electrolytes upon the zeta potential of soils and substrates has been collated, permitting an estimate of the areas in need of further elucidation. Cited are available correlations between zeta potential and suspension values, critical micelle concentration, and detergency values.

INVARIABLY as the investigator in the surfactant field delves more deeply into the surfactancy function, the factor of electrical (or ionic) charge becomes increasingly important. Initially, of course, whether the surfactant be anionic, nonionic, amopholytic, or cationic will be immediately recognizable, and frequently is sufficient information for intelligent utilization of the prospective surfactant. However, in any attempt to analyze the process of soil removal, many of the various forces involved turn out to be electrical in nature.

Perhaps the more generally recognized electrical phenomenon is the ability (or its essential lack) to ionize in aqueous solution. Nonionic surfactants frequently are assumed to be almost completely unionized, but polyoxonium compounds are believed to be formed by them [42], and other authors [18] by zeta potential measurements show them as possessing weakly cationic character. Advantage is taken of this in their quantitative estimation by precipitation with heteropoly acids, such as phosphomolybdic. Ampholytic surfactants are interesting materials, their ionization depending upon the medium in which they are used and upon the electrical charge of the surfaces with which they come into contact.

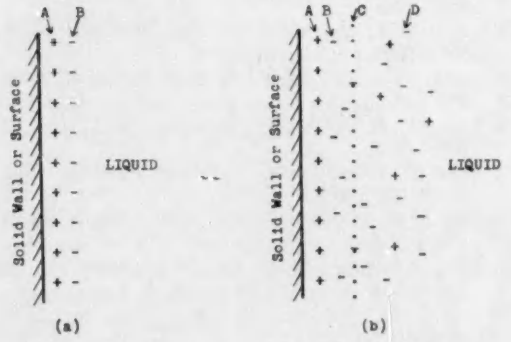

Fig. 1. Double layers. (a) Helmholtz; (b) Gouy-Freundlich; A, charges firmly attached to particle; Ba, charges of liquid layer; Bb, ions in liquid layer attached to particle; C, thickness of attached layer depending on mean offstand distance of ions from solid wall; D, diffuse ions in movable part of liquid [14].

Less generally recognized are electrical charges manifested under conditions of stress [14]:

1. Fall potential resulting from forced free fall of suspended particles through a medium without applied external electrical potential.

2. Streaming potential resulting from liquid flow against another phase.

3. Electro-osmosis, the movement of a liquid through a membrane by externally applied potential.

4. Cataphoresis, the migration of particles in a medium as a result of applied external potential.

For detergency work, only the last two phenomena are of immediate interest, and particular attention will be given only to the latter.

Helmholtz [15] theorized that an electrical double layer is formed at the surface of separation between

two phases, in simple cases analogously to an electric condenser; the potential of this system has been termed electrokinetic or the zeta potential. The assumption was that the layer consisted of two parts, one located at a monomolecular distance in the liquid medium, and movable, and the other firmly attached to the solid surface.

In Hauser's treatment [14] of this subject it is pointed out that a particle may be surrounded by an essentially rigid envelope of charges at fixed distance, and that it does not follow that this particle could be moved perfectly dry through a liquid as a result of applied potential. Gouy amended the theory to permit a gradual or diffuse potential gradient about the particle; thus the attached charged layer of the particle remains motionless, and the liquid moves, not against the solid interface, but against the liquid layer adhering to the interface when an outside potential is applied. Figure 1 clearly describes the charges involved in these systems.

Zeta potential is the difference in charge between the immovable liquid layer attached to the surface of a solid phase and the movable part of the diffuse layer in the body of the liquid. Analysis shows that to a first approximation electrophoretic velocity (or mobility) is proportional to zeta potential [19].

Measurement

Bull [5] has followed a conventional procedure in classification of the methods used in zeta potential measurement:

1. Electro-osmosis—Motion of a liquid relative to a solid under the influence of an external electric field applied tangentially to the interface.

2. Streaming potential—Movement of liquid relative to a solid in response to mechanical force applied tangentially to an interface.

3. Dorn effect (sedimentation potential)—Electric potential established by motion of a solid phase (mechanical force, usually gravity) in relation to a stationary liquid.

4. Electrophoresis—Movement of a solid phase in respect to a liquid under the influence of an electric field.

Kruyt [19] presents an excellent review of the methods used in measurement of electrophoretic velocity. Mentioned are the Hittorf method as for transport number determination, in which the concentration of the colloidal material is measured at one electrode after a given period of time; the moving boundary method, using a U tube; the Tiselius method, in which measurements are made by the "Schlieren" technique, most frequently used on biochemical materials; and the (ultra) microscope method, in which particle movement is measured using this instrument. Much of the work in the surfactant field has utilized the microscope fitted with various cells designed to minimize operational difficulties.

Zeta potentials derived by different methods are reviewed by Kruyt [19]. In some cases excellent correlation is achieved, while in others controversy still exists [39], attributable perhaps to technique involved.

Two phases with different charges in the presence of an electrical field will move oppositely to their charge. This movement is termed electrokinetic, and there is no intrinsic difference between electrokinetic motion and the movement of an ion in solution also subjected to an electric field [2]. The rate of relative electrokinetic motion of the two phases is said to be proportional to the intensity of the applied field, dependent upon the size and shape of the objects, the properties of the fluid, and on the properties of the double layer, especially upon the zeta potential. Zeta potential may be defined as the electrokinetic potential, i.e., the potential drop across the electrical double layer.

The expression for zeta potential [14] follows, in which the term v (the mobility) is measured and expressed as μ/sec./volt/cm. (μ = microns):

$$\zeta \text{ (Zeta)} = \frac{4\pi \cdot \eta \cdot v}{X \cdot D} \qquad (1)$$

in which: η = viscosity of the fluid, v = rate of electrophoretic migration, X = potential gradient, and D = dielectric constant of the medium, all in c.g.s.e. units. In this case ζ would be expressed as volts or, for whole numbers, as millivolts. Many have elected to express their data simply as mobility.

Velocity of migration of colloidal particles is independent of size, but affected, for a given applied EMF, primarily by the nature and extent of the particle charge. Therefore, any factor affecting ζ will influence the velocity of migration.

In a suspension of particles in a fluid medium, opposing forces exist [19]. Attraction of particles for one another, possibly to cause flocculation, is represented by London-van der Waals forces which, though considered as acting over a very short range

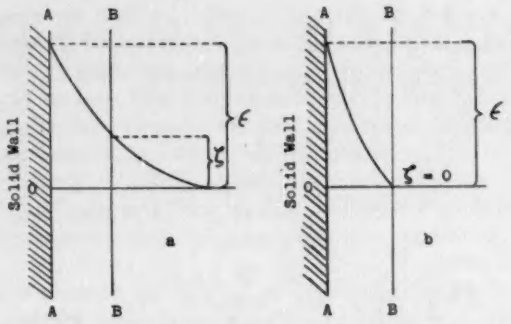

Fig. 2. a, ζ potential prior to the addition of electrolyte; b, ζ potential after the addition of electrolyte [14].

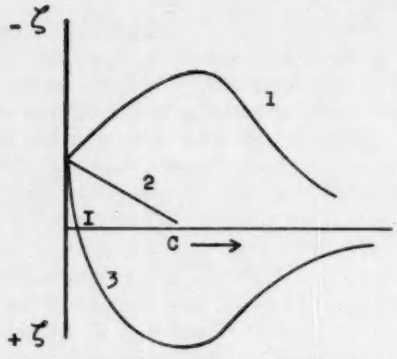

Fig. 3. Possible shapes of ζ potential–electrolyte concentration curves. I, isoelectric point; Curve 1, for weak (monovalent) electrolytes; Curve 2, for medium (divalent) electrolytes; Curve 3, for strong (multivalent) electrolytes [14].

(about 1 Å), may actually have considerably larger ranges when larger particles are involved. The range of attraction may be of the order of the particle radius—10 to 100 Å. Repulsive forces are represented by the relatively longer range double-layer charges [39] resulting from the adsorption of ions (or electrons). Stillo and Kolat [36] discussed nonelectrical repulsive forces based on the Mackor-van der Waals theory of colloid stability in nonpolar media [19A, 19B]. Adsorption of surfactant on a particle may result in repulsive forces from the decrease in entropy obtained when such surfactant-adsorbed particles approach each other. This decrease in energy causes an increase in configurational free energy leading to the repulsive force; these repulsive forces at short distances may overcome long range attractive forces between the colloidal particles. Stillo and Kolat [36] apply this concept to polar media, the decreased attractive force postulated as being due to an increase in the minimum permitted distance of approach or as an increased non-electrical repulsive force.

Disperse systems may be stabilized by three mechanisms [21]:

1. Resulting only from repulsive forces from the double layer.
2. Solvated systems (hydrated if water is the continuous medium) resulting from an enveloping sheath of solvent about the particle.
3. Combination of mechanisms 1 and 2. The latter mechanism can be converted either to system 2 by the addition of electrolyte or to system 1 by treatment to dehydrate the surface of the dispersed particle. Type 3 frequently can be flocculated only by reducing both electrokinetic potential and degree of solvation at the particle surface.

Stabilization of suspensions can be achieved by mechanism 3 above, but Adam [2] describes the process slightly differently. For similarly charged particles, energy must be expended to bring one through the electrostatic repulsion layer of the other; this in turn depends on the potential around the particle, which in turn depends on total particle charge, its density, and the dielectric constant of the fluid medium surrounding the particle. Particle charges, acting as a result of the potential they produce in the fluid, hinder the particle approach to the critical distance at which they would stick together.

In the conception of the potentials involved in suspension systems, in addition to the zeta potential there exists yet another important electrical charge, the entire surface charge, or surface potential. As reference to Figure 2 will show, the charge on the particle (surface potential) can remain unchanged while the zeta potential becomes zero.

Electrolyte Effect

It was pointed out that for electrolytes the OH^- and H^+ ions determine potential [19, 23], a small increase in the OH^- ion increasing the negative potential, H^+ ions causing it to decrease. At increased concentrations all electrolytes cause a decrease in zeta potential. However, at very low electrolyte concentrations zeta becomes nearly independent of concentration on the log scale, while at higher concentrations a linear relationship is found [19] when:

$$\zeta = A - B \log C \text{ (concentration)} \quad (2)$$

A and B representing constants.

In systems where unaltered water is the continuous medium, the zeta potential is strongly negative; most particles, even air or neutral oil, are negatively charged. The cause [20] of the electronegative charge of the great number of inert materials is said to be sought in the adsorbed layer of oriented water molecules which apparently attract anions to the interfacial side of this layer, giving rise to an adsorption potential.

Figure 2, by Hauser [14], depicts the appearance of the potential curve before and after the addition of electrolyte. It is obvious that the double layer has been somewhat compressed as a result of electrolyte addition, zeta becoming zero.

The effects of electrolyte on zeta potential may be summarized as follows:

1. All anions tend to make particles negative and cations to make them positive.

2. At relatively higher electrolyte concentration, all electrolytes effect a decrease in zeta potential.

3. Anions influence a positive increase in zeta potential in preference to cations. Cations decrease the negative potential.

4. Negative zeta potential is primarily influenced by cations. The greater the valency of the cation, the greater the decrease in negative zeta potential, conforming to the Schulze-Hardy rule. Order of cation effectiveness [40] is:

Tetravalent > Trivalent > Divalent > Monovalent

K < Mg < Ca < Sr < Ba < Al < Th----------H

Bancroft [3] lists as possible exceptions to this rule the specific character of the anion, cation, suspension, and hydrogen ion concentration.

5. Adsorbability of anions follows the Hofmeister or lyotropic series [40]:

SO_4 < F < NO_3 < Cl < Br < I < CNS <-------OH

6. Hydration or solvation affects the character of the dispersion, those approaching H^+ ions the least.

Hauser's [14] illustration, Figure 3, demonstrates the possible zeta potential curve shapes with concentrations of various electrolyte valencies.

Temperature Effect

Powney and Wood [28], working with suspensions of Nujol and paraffin wax, found that change of mobility with temperature in the range of 25–60° C. depended on the viscosity change of the water according to the simple relationship $\mu_1\eta_1 = \mu_2\eta_2$, where μ represents mobility and η the viscosity of the water. Their data are shown in Figure 4.

Others [38], in consideration of temperature effect, have used information showing that variation in viscosity by temperature produces a corresponding velocity change of the particles such that $\eta \frac{(V)}{(X)}$ is a constant, where η = viscosity, V = particle velocity, and X = potential gradient. If $\eta \frac{(V)}{(X)}$ is constant, then ζD also is constant, and since D (dielectric constant of the medium) varies with temperature, then ζ must also vary. Hence the value of ζ may be calculated for any temperature for which D is known (Equation 1), utilizing the value $\mu \cdot \eta$ from one temperature only. In calculation from 25 to 60° C. all values would shift by the same percentages, and the relative order would remain the same. See Figure 4, obtained experimentally, for soap solutions which show characteristic curve inflections attributable to adsorption phenomena.

Zeta potential–temperature curves were obtained [32] for acetate rayon in KCl solutions from 0.01 to 0.0001 N. A linear increase in ζ was found with temperatures from 20 to 80° C.

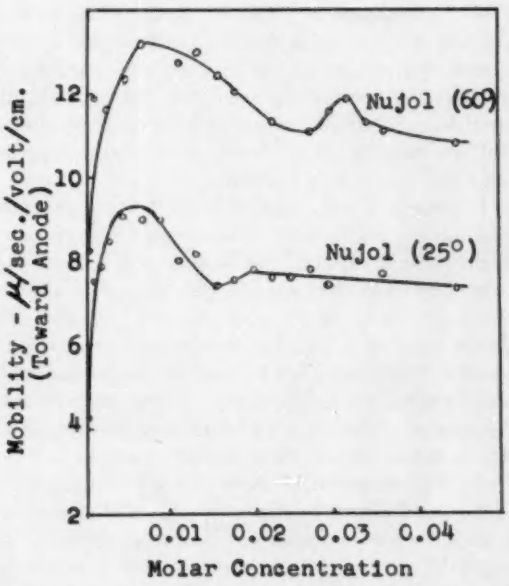

Fig. 4. Temperature effect. Mobilities in sodium laurate solutions (0.01 M, 0.222%) [28].

TABLE I. Electrokinetic Mobilities of "Soils" in Water

Particles	Mobility, μ/sec./volt/cm.	Zeta potential, millivolts	Ref.
Quartz	−3.00	−44	13
Iron oxide	−1.9	—	18
Ferric oxide	+3.00	+44	13
Ferric oxide	−2.1	−28	38
Iron	+1.90	+28	13
Air bubbles	−4.00	−56	13
Oil (emulsion)	−4.30	−60	13
Paraffin oil	−7.1	−86	38
Nujol	−4.2	—	28
Nujol	−3.4	—	24
Nujol	−4.2	—	27
Cottonseed oil	−6.1	−74	38
C Black	−4.5	−60	38
C Black	−1.7	—	31
Molacco carbon	+2.1	—	7
Lampblack	−3.2	—	18
Lignite	−2.3	—	18
Excelsior carbon	−1.8	—	7
Carbon	−2.2	—	37
Water-insoluble dye	−4.6	−62	38
Ilmenite	−2.3	—	28
Clay	−3.1	—	20
Calcium laurate	−3.8	—	28

Mobility Values in Water and Electrolyte Solutions

"Soil" in Water

The mobility values for a variety of potential "soils" are shown in Table I. Kruyt [19], in considering the forces involved in a suspension system, stated that the repulsion between two particles is greater, the greater the zeta potential between the particle and solution. Since mobility and zeta potential are roughly proportional, either figure may be used for comparison purposes.

In considering the data of Table I, some generalizations are warranted. These data come from a variety of sources and have been determined and calculated by more than a single system, using materials generally rather poorly characterized. Though the data are rather qualitative, they nevertheless suggest possible trends, and can be used in comparison with similar values for textile fibers. When one compares the several values for mineral oil, considerable variation is noted, but where a common material such as Nujol was measured by three separate investigators, rather good concordance was obtained. For carbon, a rather wide variation in values is obtained, as might be predicted from the variation possible in this material. Iron oxide presents a picture comparable to carbon, for the same reasons.

There are insufficient data for any single series of similar materials to permit other than a qualitative characterization.

"Soil" in Electrolyte Solutions

Collected in Table II are values for the mobilities of carbon, ilmenite, mineral oil, and clay particles in solutions of a number of electrolytes and from a variety of sources. Again, method of measurement and source and variation in materials probably have considerable bearing upon the quantitative character of the data.

For suspended carbon particles measured in the same strength of electrolyte (NaOH or Na_2CO_3), rather wide variation in mobility exists, undoubtedly due to the specific carbon under measurement. For a given carbon measured by the same investigator for a series of electrolytes, it could be expected that the values should be comparable, and differences in effect produced should be valid. Several examples are given in Table III. These examples, developed by the same method in each case, point up the marked differences in results dependent upon the carbon used.

In the series of essentially neutral electrolytes tested and where comparable concentrations have been used, monovalent anions impart lower mobilities to soil particles than are imparted by those polyvalent in character. The same is true and to a more marked degree with polyvalent cations (and here the charge can be reversed).

In general, alkaline electrolytes are more effective in increasing mobility than are neutral electrolytes of the same anion valency. For example, hydroxyl ions may form hydrogen bonds with oxygen complexes on the surface of the soil.

The data indicate that mineral oil droplet mobilities are increased more by available OH^- ion than by other anions, and are more radically affected by valency of the cation than are other soils.

Kling and Lange [18] measured the mobility of carbon particles in solutions of essentially neutral electrolytes possessing polyvalent anions; as is shown in Figure 5, the mobility with sodium chloride remains essentially unchanged by concentration, while the curves for low alkalinity phosphate salts show maxima in about 10^{-3} N solutions, the effectiveness increasing slightly with increasing valency of the phosphate ion. A similar attempt to differentiate between the normally alkaline salts shows maxima

between 10^{-3} and 10^{-2} *N*, but the maximum is maintained well for increasing concentration. This is shown as a composite in Figure 5. In any case, the highly polyvalent glassy (meta) phosphate provided the highest mobility. The "neutral" salts tested were NaCl, Na_2HPO_4, $Na_2HP_2O_7$, and $(NaPO_3)_x$; the alkaline compounds were NaOH, Na_2CO_3, Na_3PO_4, $Na_4P_2O_7$, and $Na_5P_3O_{10}$.

Fibers in Water or Electrolyte Solutions

The available data are rather scarce and frequently refer only to water or simple electrolytes such as KCl or NaCl. Table IV shows a variety of fibers, but only for cotton has any extensive investigation of detergent builder electrolytes been made. It becomes immediately apparent that the zeta potential for cotton varies widely. Briggs [4] early pointed out variance in zeta potential with the history of the cellulose sample and obtained values ranging from 8 to 21 millivolts. Others [30] demonstrated that zeta potential for cellulose is decreased with chemical change, as when the carboxy content is increased. More recently others [32] have emphasized the importance of the knowledge and control of pretreatment when textile fibers are to be subjected to mobility measurements.

Cotton which has been mercerized has a relatively high zeta of −38; with variation in mercerization even this value probably could have been altered downward. The more chemically reactive the fiber

TABLE III

Salt	Conc.	μ	Ref.	Salt	Conc.	μ	Ref.
NaOH	.01 *N*	−1.7	37	NaOH	0.01 *N*	−5.1	18
Na_2CO_3	.003 *M*	−1.2		Na_2CO_3	0.01 *N*	−5.0	
Na_2SiO_3	.004 *M*	−1.7		Na_3PO_4	0.01 *N*	−4.7	
				$Na_4P_2O_7$	0.01 *N*	−5.0	
				$Na_5P_3O_{10}$	0.01 *N*	−4.9	

TABLE II. Electrokinetic Mobility of Various "Soil" Particles in Electrolyte Solutions

Salt	Conc.	Particle	Mobility, μ/sec./volt/cm.	Zeta potential, millivolts	Ref.
NaCl	0.01 *N*	Carbon	−3.6	—	18
Sodium acetate	0.0036 *M*	Carbon	—	−41	38
Sodium sulfate	0.0036 *M*	Carbon	−4.7	−57	38
Na_2HPO_4	0.01 *N*	Carbon	−4.7	—	18
$Na_2H_2P_2O_7$	0.01 *N*	Carbon	−4.6	—	18
$(NaPO_3)_x$	0.01 *N*	Carbon	−5.3	—	18
$K_4Fe(CN)_6$	0.0036 *M*	Carbon	−5.0	−60	38
NaOH	0.01 *N*	Carbon	−5.1	—	18
	0.01 *N*	Carbon	−1.7	—	37
Na_2CO_3	0.01 *N*	Carbon	−5.0	—	18
	0.003 *M*	Carbon	−1.2	—	37
Na_3PO_4	0.01 *N*	Carbon	−4.7	—	18
	0.0036 *M*	Carbon	−5.2	−63	38
Na_2SiO_3	0.004 *M*	Carbon	−1.7	—	37
$Na_4P_2O_7$	0.01 *N*	Carbon	−5.0	—	18
$Na_5P_3O_{10}$	0.01 *N*	Carbon	−4.9	—	18
NaCl	0.012 *N*	Ilmenite	≤ -2	—	28
Na_2CO_3	0.012 *N*	Ilmenite	−3.2	—	28
Na_2SiO_3	0.012 *N*	Ilmenite	−3.9	—	28
NaCl	0.01 *N*	Mineral oil	< -2	—	27
KCl	0.01 *M*	Mineral oil	—	−46	25
$K_4Fe(CN)_6$	0.01 *M*	Mineral oil	—	−70	25
$BaCl_2$	0.01 *M*	Mineral oil	—	−18	25
$AlCl_3$	0.01 *M*	Mineral oil	—	+ 2.5	25
$NaHCO_3$	0.01 *N*	Mineral oil	−4.7	—	27
$Na_4P_2O_7$	0.01 *N*	Mineral oil	−5.7	—	27
Na_2CO_3	0.01 *N*	Mineral oil	−7.3	—	27
Na_2SiO_3	0.01 *N*	Mineral oil	−8.1	—	27
NaOH	0.01 *N*	Mineral oil	−8.8	—	27
Water		Clay	−3.1	—	20
Na_2SO_4	0.0015 *N*	Clay	−2.9	—	20
Na_2HPO_4	0.0015 *N*	Clay	−3.9	—	20
$K_4Fe(CN)_6$	0.0015 *N*	Clay	−4.0	—	20
NaOH	0.0015 *N*	Clay	−4	—	20
$FeCl_3$	0.0015 *N*	Clay	+0.3	—	20

the more susceptible it is to pH effect, the amphoteric fibers obviously showing greatest variation in this respect. Wool, for example, in distilled water may have zeta potentials of −38 to −48, while at pH 11 the value rises to −62. Nylon at pH 3 has a zeta of −1, and at pH 11 the zeta becomes −60. Though incomplete data are available for silk, it too should conform to this general picture. Pyridinized cotton and rayon have relatively high positive zeta potentials of 19 and 9 respectively. Though not shown, these probably would change to moderately low negative zeta values in alkaline solutions.

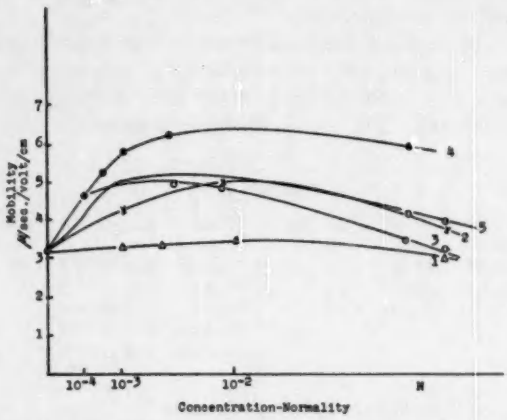

Fig. 5. Mobility of carbon black in electrolyte solutions [18]. 1—NaCl; 2—Na_2HPO_4; 3—$Na_2HP_2O_7$; 4—$(NaPO_3)_x$; 5—approximation of alkaline salts of Curves 2, 3, and 4.

In distilled water the fibers may be arranged according to zeta potential in the following approximate order:

Silk	−1
Viscose	−2 to −8
Nylon	−1 downward
Cotton	−1 to −38
Acetate	−36
Wool	−38 to −48

No data appear available to show the orderly effect of individual detergent builders upon mobility of the "soil" particles, the emphasis apparently having been placed on the surfactant-builder systems, to be discussed later.

The available essentially comparable data for cotton and for several soils are shown, as selected from Tables I, II, and IV, in Table V. The mobility

TABLE IV. Electrophoretic Mobility of Fibers in Solutions of Various Electrolytes

Fiber	Salt	Conc.	Mobility, μ/sec./volt/cm.	Zeta potential, millivolts	Ref.
Cotton	Water	—	−1.9	—	37
	Water	—	—	−1.3	7
	Water	—	—	−15	16
	Water	—	—	−10	6
	Water	—	—	−38	33
	Water	—	—	− 1.9	37
	KCl	0.01 *N*	—	−25	32
	KCl	0.01 *M*	—	−12	6
	NaCl	0.01 *M*	—	−18	33
	NaOH	0.01 *M*	−1.1	—	37
	Na_2CO_3	0.003 *M*	−1.3	—	37
	Na_2SiO_3	0.005 *M*	−0.6	—	37
	$BaCl_2$	0.01 *M*	—	−60	6
	$AlCl_3$	0.01 *M*	—	−34	6
Mercerized cotton	Water	—	—	−38	16
Wool	Water	—	—	−48	16
	Water	pH 11	—	−62	33
	KCl	0.01 *N*	—	−38	32
Nylon	Water	pH 3	—	− 1	33
		pH 11	—	−60	33
Silk, degummed	Water	—	—	− 1	16
Viscose rayon	Water	—	—	−1.7 to −8	16
	KCl	0.01 *N*	—	−14	32
Cuprammonium rayon	Water	—	—	− 5	16
Acetate rayon	Water	—	—	−36	16
	KCl	0.01 *N*	—	−16	32
Pyridinized cotton	Water	—	—	+19	16
Pyridinized rayon	Water	—	—	+ 8.6	16

ranges shown for carbon reflect both the carbon chosen and the technique of measurement. The greatest increase in mobility is shown by the electrolytes for mineral oil, ilmenite next, and carbon least. Further tentative conclusions based on the data might be attempted, but would prove unreliable in the face of practical knowledge. Needed are more data developed on a systematic basis under controlled conditions of measurement.

Surfactants and Mobility Values

Anionic Surfactants

As in many other fields of surfactant measurement, soaps have been most widely investigated. The most complete data for suspensions are those of Urbain and Jensen [38]. Figure 6 is taken from their work and shows the proportional character of the mobility and zeta potential curves previously discussed. These curves were prepared at a temperature sufficient to provide solubility for the normally very viscous stearates and at concentrations approaching those used in normal detergency operations (about 0.1%).

While surfactant–soil systems give valuable information, measurements made under nearly identical conditions with the medium (or substrate) from which the soil might be removed is equally as valuable. Such data for a single soap, a low titer commercial product, follow [37]:

Soap, %	Mobility, μ/sec./volt/cm.	
	Carbon	Cellulose
Water	2.16	1.90
0.05	2.80	5.65
0.1	3.36	5.55
0.2	3.27	4.70

(The movement of particles is toward the anode.) An interpretation of these values and their significance is now important when the soil/substrate media are to be compared. Powney and Wood [18] stated that those particles with high zeta potential will repel each other more strongly than those of lower potential, thus providing a relatively more stable system. Relative to mineral oil suspensions, Powis [25] indicated that a minimum zeta potential of 30 millivolts is necessary for the formation of relatively stable oil-in-water emulsions. Urbain and Jensen [38] found that more stable suspensions of either carbon or mineral oil were obtained with relatively high zeta potential. Goette [11] stated that

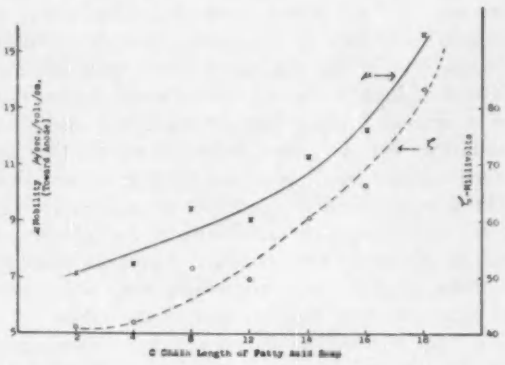

Fig. 6. Carbon suspended in soap solutions [38]; 0.0036 *M* at 75° C.

TABLE V. Mobilities of Selected Electrolytes, Soils, and Cotton Particles

Mobilities all toward anode and are in μ/cm.μvolt/sec.

Electrolytes	Cotton	Soil particles		
		Carbon	Mineral oil	Ilmenite
Water	1.9	2.2	4.2	2.3
NaOH	2.1*	1.7	8.8	—
Na_2CO_3	1.3*	1.2	7.3	3.2
Na_2SiO_3	1.5*	1.7	8.1	3.9

* [33] at about 0.003 *M* concentration.

for like zeta potentials between soil and solution, and between substrate and solution, the higher the zeta potential the greater the detergent effect. Stubblebine [37] felt that mutual repulsion occurred only when two similarly charged particles had nearly the same value; i.e., for best detergency the charges on soil and fiber should be nearly the same, and both as highly negative as possible.

In the data given above for soap, the interpretation could rightly be made that the more effective removal of carbon from cellulose would occur at 0.2% rather than at lower concentrations. By interpretation of the data in the same way, from Table VI, one would decide the best combination for sodium carbonate is the 54 soap-46 builder mixture, while for sodium metasilicate, the 4 and 9% additions should give optimum results, although the 2% metasilicate addition shows better results than even the best sodium carbonate combinations.

The curves of Figure 7 show the effect of added electrolyte upon the initial mobility of either carbon or iron oxide particles in solutions of potassium

laurate. These curves show the effectiveness of sodium carbonate in increasing particle mobility. Comparison of the surfactant alone with the surfactant–sodium carbonate combination shows that, at a critical solution concentration, the curve for surfactant without added electrolyte equals, then becomes greater (more negative) than the combination. The adverse effect of electrolyte at sufficiently high concentration may be attributed to compression of the double layer with resultant decreased mobility.

Some generalizations concerning soap which may or may not apply to other surfactants follow [38]:

1. The relationship between soap, carbon chain length, and mobility are in the same general order for Nujol and carbon.

2. Mixtures of soaps show no essential difference in the effects observed; zeta potentials are of the same order of magnitude as those for the pure surfactants.

3. No real differences in mobility are evident between sodium or potassium soaps.

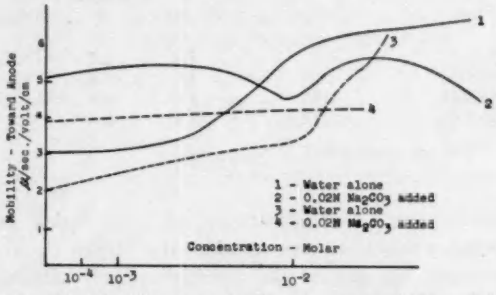

Fig. 7. Mobility in potassium laurate solutions [18]. Curves 1 and 2—carbon black particles; Curves 3 and 4—iron oxide particles.

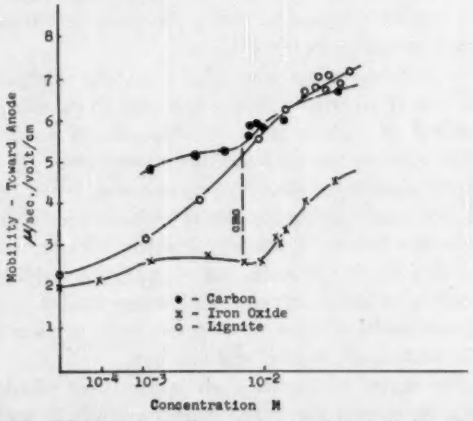

Fig. 8. Mobility in sodium dodecyl sulfate solutions [18].

4. Alkalinity of soaps is alone insufficient to account for their large effect on the zeta potential of carbon particles suspended in their solutions.

A series of diester sulfosuccinate salts was examined [24]:

Aerosol OT—Di-2-ethylhexyl sodium sulfosuccinate
Aerosol MA—Di-2-methylamyl sodium sulfosuccinate
Aerosol AY—Di-2- and 3-methyl-1-butyl sodium sulfosuccinate

It was shown that mobility of the Nujol droplets in solutions of these surfactants does not increase in the regular order observed for increase in chain lengths for soaps, and that the mobility values at a maximum approximate the C_{10} to C_{12} fatty acid soaps. (However, these were carbon suspensions, not Nujol.)

The mobility of carbon, iron oxide, and lignite particles in solutions of sodium dodecyl sulfate were measured as shown in Figure 8. Since lignite is a very impure form of carbon, it might be expected that the carbon and lignite curves might approximate one another. In view of the widely variant characteristics of carbons from different sources, this occurrence is rather unusual. Iron oxide shows a considerably lower mobility than the other two materials. It is important that two curves show an inflection at the critical micelle concentration (cmc) of the surfactant, and this occurrence with fibers is duplicated in subsequent exhibits.

The systematic study by Kling and Lange [18] included mobility measurements of carbon suspensions in combinations of sodium dodecyl sulfate with neutral or alkaline surfactant builders (Table VII).

TABLE VI. Soap–Builder Mixtures [37]

Soap, %	Builder, %	Na_2O in builder, %	Mobility, μ/sec./volt/cm. Carbon	Cellulose
Na_2CO_3 builder				
85	15	0.01	−3.36	−5.55
74	26	0.02	−2.20	−3.30
54	46	0.05	−2.21	−2.23
Na_2SiO_3 builder				
98	2	0.01	−3.42	−3.15
96	4	0.02	−2.15	−2.08
91	9	0.05	−2.39	−2.36

Solution concentration of soap 0.1% + builder.

TABLE VII. Carbon Suspensions with Sodium Dodecyl Sulfate Built with Various Salts [18]

Salt	Mobility × 10^4 (toward anode) 0.01 *N* Salt 0.01 *M* WA*	0.01 *N* Salt 0.02 *M* WA	0.1 *N* Salt 0.02 *M* WA
Surfactant (alone)	4.6	5.9	
NaCl	5.4	5.2	
Na_2SO_4	5.4	—	
Na_2HPO_4	5.4	5.4	
$Na_2HP_2O_7$	5.9	5.5	
$(NaPO_3)_x$	5.8	5.1	
NaOH	4.8	—	
Na_2CO_3	5.7	5.3	5.8
Na_3PO_4	4.9	4.3	
$Na_4P_2O_7$	5.2	5.0	
$Na_5P_3O_{10}$	5.5	5.5	
$MgCl_2$	3.9		

* WA = Sodium dodecyl sulfate.

TABLE VIII. Moving Boundary Method [10]

Mobility (μ/sec./volt/cm.)

Composition		Particles: None	Carbon	Cotton
A – Sodium tripoly-phosphate	0.08%	—	22–24	6–7
A – Sodium carbonate	0.04%			
A + 0.12% ABS*		—	21–22	—
A + 1% ABS		22–27	—	—

* Sodium dodecyl benzenesulfonate—Nacconol NRSF.

In explanation for the low reduction in mobility at 0.02 *M* concentration of surfactant, it was suggested that the carbon particles are thickly coated with a layer of adsorbed long chain ion, and that this, in the presence of alkaline salts, results in the reduction in mobility noted.

Paraffin wax in 0.1% solution of sodium tetradecyl sulfate has a mobility of 12.5–13.6 toward the anode [28].

The zeta potentials for nylon [33] varied similarly to the values found by Neale and Peters [22], but their negative zeta potentials were lower in alkaline solutions. The adsorption of dodecyl sulfate was greater at pH 3 than at pH 11, and the reverse was true for the dodecyl pyridinium ion.

Figure 9 indicates the increased zeta potential of cotton fibers at the lower solution concentrations, the marked deflection at cmc, and the sharply increased values at concentrations above cmc; their implications are discussed in the section on correlation of mobility, zeta potential, and cmc.

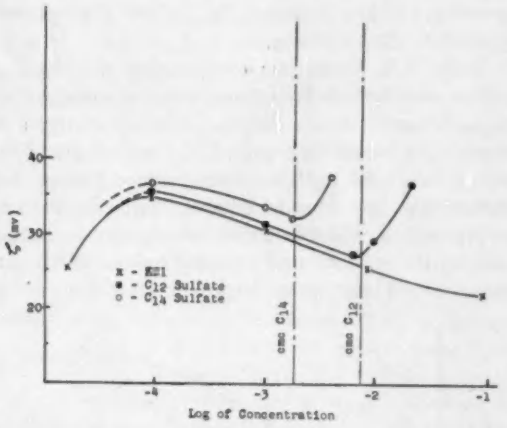

Fig. 9. Cotton zeta potential values in sodium alkyl sulfate solutions [12].

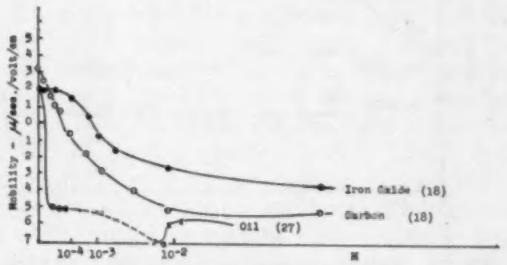

Fig. 10. Mobility of particles in dodecyl pyridinium chloride solutions.

Sodium alkylbenzene sulfonate (Figure 11) shows a continued increase in mobility of carbon particles with increase in concentration. The general increase in mobility approximates that of sodium laurate but appears slightly lower than sodium dodecyl sulfate. Table VIII shows a comparison of cotton and carbon mobilities in a builder mixture, and with this mixture plus another example of sodium alkylbenzene sulfonate. Addition of the surfactant had only slight effect on carbon particle mobility, but again the data are not adequate.

Cationic Surfactants

The outstanding characteristic of cationic surfactants, of course, is the positive charge imparted by them to suspended particles, as shown in Figure 10, taken from two sources. Goette [11] indicated that detergency for cationic agents begins to appear at concentrations higher than about 1.0%. The reason for this is apparent in the shape of the curves;

greatest mobility (toward the cathode) occurs beyond this concentration.

Table XII shows the comparative mobilities of cotton and two carbons possessing opposite polarities, Molacco carbon being positively charged in water. As would be expected, the magnitude of the charge increases with increasing concentration, but cotton does not show as great a charge increase as either carbon. The fact that the charges on cotton and on the carbons never closely approach one another would suggest a degree of attraction rather than repulsion, such that some soil might be removed from cotton, but a high degree of detergency is never attained.

Stanley [33] determined the zeta potential of wool in dodecyl pyridinium bromide solutions as a function of pH. Between pH 6 and 3, zeta falls almost linearly with decreasing pH. A definite change of slope occurs at pH 7, and zeta rises slowly as alkalinity is increased. He also discussed the relationship between the chemical constitution of wool and the changes which occurred in the presence of the cationic agent under the conditions given.

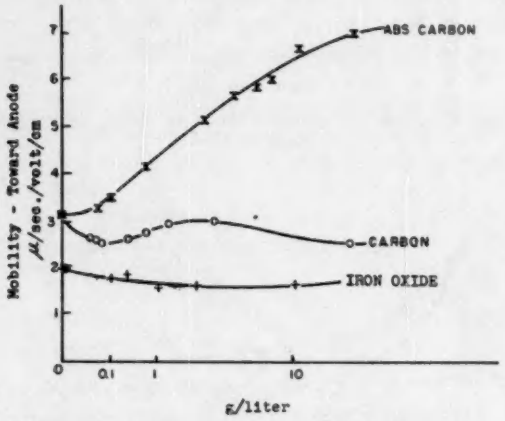

Fig. 11. Mobility–concentration curves [18]. ABS Carbon—sodium alkylbenzene sulfonate; Carbon—dodecyl alcohol-EO adduct; Iron oxide—dodecyl alcohol-EO adduct.

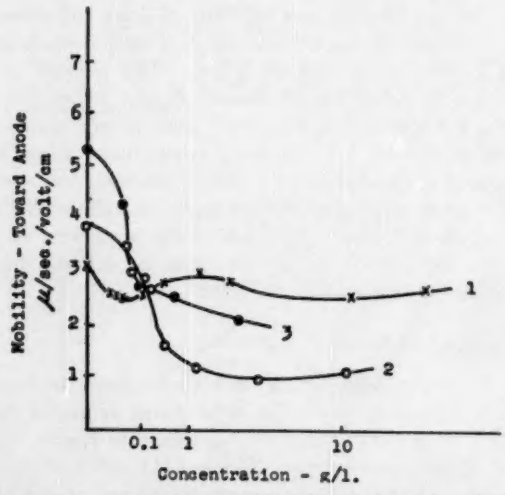

Fig. 12. Carbon black mobility in solutions of nonionic surfactant [18]. 1—in water; 2—0.01 *N* K_2SO_4 added; 3—0.02 *N* Na_2CO_3 added.

Nonionic Surfactants

The data for nonionic agents are relatively scarce. Figure 11 shows the relatively low initial mobility of carbon or iron oxide particles in solutions of the adduct of a C_{12} alcohol with 15 moles of ethylene oxide [18]. The negligible change in the mobility curves with concentration seems characteristic of this class of product.

Figure 12 appears to confirm the relatively low zeta potential values of carbon particles, even though electrolytes which normally increase zeta for anionics are added. An initial increase in value at very low solution concentrations follows the anionic picture, but increasing concentrations of surfactant at constant electrolyte concentration result in reduced zeta values, approaching zero, particularly for the neutral electrolyte. These data seem to indicate that "building" nonionic with electrolytes would result in lowered surfactancy. Since builders actually effect an improvement in detergency, factors other than zeta potential evidently are more indicative of activity.

Lissapol N (alkylphenol-ethylene oxide adduct) solutions at pH 3 and pH 11 were tested with wool [33]. At pH 3, essentially no effect on zeta was produced over a concentration range of 0–0.17%,

TABLE IX. Nonionic Surfactants

Concentration, %	Mobility (toward anode), μ/sec./volt/cm.	
	A	B
0	3.2	1.8
0.01	2.5	2.0
0.1	2.9	2.0
1.0	2.8	1.9

A—C_{12} alcohol + 15 moles ethylene oxide [18].
B—Renex (presumably Tall oil with about 10 moles ethylene oxide) [7].

while at pH 11 the initial zeta of wool in water of −70 mv. was reduced to a level of −23 mv. at about 0.015% concentration, and this zeta level continued to 0.15% concentration. Similar tests of nearly pure *p*-octylphenyloctaglycol ether gave very similar results at pH 11.

The comparison of two different kinds of nonionic surfactants given in Table IX emphasizes the relatively low mobility levels of these compounds. Since good detergents can be formulated from nonionic agents, and because zeta potential has such strong bearing upon surfactancy, the very sparse data need to be amplified to explain this apparent discrepancy in the facts, though factors other than zeta potential may be important.

The zeta potentials of a number of fibers in water and the three types of surfactants are summarized in Table X from the excellent curves developed by Kling and his coworkers [32]. Kling [17] characterized these data as follows: the negative charge on fibers in water can be increased by anionic surfactants, remains unchanged with nonionics, and changes to a positive charge at higher concentration of cationics. In the washing process an increase in the negative charge of both fiber and soil is produced by anionic detergents, which increases their repulsion for one another and improves detergency. Redeposition of soil on fiber occurs with cationic agents, even to the extent of redistribution of the soil from a dirty fabric to a clean one in the same solution. Zeta potential fails to explain the detergency of nonionic surfactants.

Correlation Between Zeta Potential and Other Phenomena

Suspension Values

Fall [9] mentioned the suspending ability of sodium silicates, sodium carbonate, and trisodium phosphate for MnO_2 and other soils, but found that the rate of settling decreased with concentration up to a certain value, then increased upon further increase in concentration of the alkaline salts. These maxima generally occurred at relatively low solution concentrations, undoubtedly as a result of their effect upon anion adsorption by the particle and suppression of the thickness of the double layer, as schematically shown in Figure 2. Zeta potential then is a good measure of the effect of electrolytes upon suspension stability and is frequently mentioned in the literature on this subject.

Fong and Ward [10] measured the sedimentation velocity of carbon black particles referred to standard water at 20° C. and unit centrifugal field. The sedimentation constant (expressed as Svedberg units $\times 10^{-13}$ sec.) was measured in an ultracentrifuge. The data of Table XI show that carbon sediments less rapidly in the presence of the alkaline builders than in their absence and that dodecylbenzene sodium sulfonate has essentially little effect on these results.

Another investigator [7] has attempted to demonstrate the relationship between mobility and suspendability, using carbon as the suspended agent and cationic surfactant Hyamine 1622 as the surfactant. Table XII for Molacco black (the carbon in question) from mobility data would suggest that higher concentrations of surfactant might improve mobility (even though moving toward the cathode), but suspension values are at a maximum at about 0.25% solution concentration and become zero again at 3.0%. This stability curve resembles that of Hyamine 1622 for manganese dioxide [12], becoming maximum at about 0.2% and zero again at about 0.9%. Both this carbon and manganese dioxide are positively charged, and both reacted in the same general manner to the cationic agent in suspendability. Presumably they would have given the same general reaction to mobility, though probably with slight differences in magnitude.

Ray and Hutchison [31] measured both mobility and carbon suspending power in dilute soap solutions. In both cases, approximately maximum values were achieved at about 0.1% concentration, though

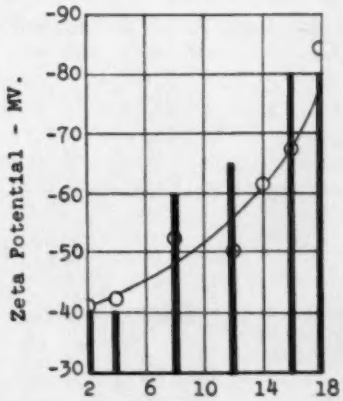

Fig. 13. Zeta potential and suspension values [38]. Carbon particles immersed in 0.0036 *M* soap solutions. Bars represent relative order of suspension stability. Curve represents zeta potentials.

TABLE X. Fibers in Surfactant Solutions [32]

Zeta Potentials in Millivolts
Potentials Attained over a Broad Concentration Range

Water		Alkyl sulfate		Nonionic 0.0001–0.1%		Nonionic 1%		Cationic	
ζ	Fiber	ζ	Fiber	ζ	Fiber	ζ	Fiber	ζ	Fiber
−52	PVC	−80	wool	−48	wool	−30	silk	+43	acetate
−51	acetate	−80	Perlon	−45	PVC	−29	PVC	+43	wool
−48	wool	−60	PVC	−43	acetate	−27	acetate	+35	Perlon
−38	Perlon	−60	acetate	−35	silk	−27	wool	+31	silk
−29	viscose	−50	silk	−34	Perlon	−26	Perlon	+29	PVC
−28	silk	−35	cotton	−28	viscose	−23	cotton	+23	viscose
−27	cotton	−30	viscose	−27	cotton	−18	viscose	+ 4	cotton

TABLE XI. Mobility and Sedimentation Values for Carbon [10]

Mobility—μ as μ/sec./volt/cm.
Sedimentation—Svedberg units × 10^{-13} sec.

Material	Mobility	Sedimentation constant
1) Water—no detergent or electrolyte, pH 8.5	—	1350
2) Sodium tripolyphosphate 0.08%, Na_2CO_3 0.04%	22–24	1130
3) 2 + 0.12% Nacconol NRSF	21–22	1140

TABLE XII. Cationic Surfactant [7]
Mobility and Suspendability

Conc. of Hyamine 1622,* %	Suspended agent—mobility† Cellulose—0.2%	Carbon—0.2% Excelsior	Carbon—0.2% Molacco	Suspended agent—suspendability g/l. Molacco carbon
0	−1.3	−1.8	+2.1	0.1
0.001	+0.30	—	—	—
0.01	+1.8	+3.8	+6.2	1.7
0.10	+2.8	+6.8	+8.5	1.9
0.25	—	+7.3	—	—
0.5	—	—	+9.5	1.9
0.75	—	+7.0	—	—
1.0	+3.0	—	—	1.8
1.5	—	+7.6	+8.8	0.2
3.0	+3.2	+7.9	+9.2	0.0

* Diisobutylphenoxyethyldimethylbenzylammonium chloride monohydrate 100%.
† μ/sec./volt/cm.

the mobility curve had the sharpest change in slope up to 0.05%. The two curves both show flat maxima beyond the 0.1% point, and their resemblance to typical adsorption isotherms was pointed out by these investigators.

A comparison [38] of zeta potential and relative stability of carbon particle suspensions is shown in Figure 13, where it becomes apparent that stability and zeta potential as factors of carbon chain length in soaps are essentially proportional and are improved as the carbon chain length approaches 18.

Reference to Table II will show that mineral oil suspensions generally seem to have higher mobilities than solid particles; in reviewing mobility and stability of mineral oil droplets, Urbain and Jensen [38] found references indicating that oil-in-water emulsion stability depended upon the value of the electric charge: the higher the (negative) value the more stable the emulsion.

While the numerical values of zeta are not always very much greater in the presence of a surfactant, it is entirely possible that a certain critical potential must be reached to form a relatively stable suspension. However, this critical potential is said probably to vary with the kind of material and size of the particles, in accordance with Stokes' law [38].

Critical Micelle Concentration

Surfactant solutions display optimum surface characteristics at the critical concentration for micelle formation (cmc). Presence of surfactant in solution results in orientation of the surfactant at interfaces, and at sufficient concentration is followed by association with one another.

The minima in the Nujol curves (Figure 4) for sodium laurate solutions reflect the cmc values for this compound, being approximately 0.35% at 25° C. and 0.6% at 60° C. [28]. A minimum for ilmenite is also found at 0.35% at 25° C. That changes

for both kinds of particles occur at the same concentration is related to a solution change—aggregation to form micelles. Similar inflections in the mobility curves for sodium tetradecyl sulfate suspensions of Nujol and ilmenite are found to correspond to cmc. Important to these observations is that particle nature does not determine the position of the mobility inflection.

The assumption that change of viscosity is the only factor involved in change of mobility from 25° to 60° C. was demonstrated as incorrect, as the observed mobilities were only 65% of the theoretical value. Hence, temperature increase caused decrease in adsorption of the long chain ions with consequent reduced mobility over theory (and reduced cmc). Powney and Wood [28] explained the fact that ilmenite particles suspended in water had only half the mobility of oil droplets whether in sodium laurate or sodium tetradecyl sulfate solutions, by assuming that with ilmenite particles the adsorbed long chain ions were oriented oppositely to those on Nujol droplets, the polar heads toward the ilmenite particle (thus becoming essentially hydrophobic in character). Inability of the monofilm-coated ilmenite particle to further adsorb another surfactant layer and thus attain a mobility value characteristic of oil droplets was explained as possibly due to some specific restriction in forming bimolecular film. Thus, change in mobility with increase in temperature is dependent not only upon change in viscosity of the dispersion medium but also upon the degree and type of adsorption at interfaces. In general, the relationship between carbon chain length and mobility are in the same general order for Nujol as for carbon particles [38].

Electrolytes when added to surfactant solutions cause reduction in cmc values, but in bringing about this reduction they can reduce the amount of surfactant necessary for increase in mobility [28]. This is attributed to increased adsorption by oil of the surfactant; however, the charge of the double layer and the extent of gegenion associated with the long chain ion also are affected by the cation introduced.

The inflections noted in the curves of Figure 9 at the points of critical concentration for the surfactants are undoubtedly explainable upon the basis that the zeta potential of the fibers ceases to increase or drops slightly because association of the molecules of the surfactant starves the solution of available surfactant ions, or actually sequesters some already adsorbed to the fiber. The increase in mobility once the cmc has been reached indicates the availability of long chain ions (and associated gegenions) for adsorption to the fiber, with consequent increase in zeta potential. Powney and Wood [27] propose the following explanation for the inflections of the mobility–concentration curves at the critical concentration for the surfactant. The first rise of mobility to a maximum is attributed to the adsorption of single long chain ions. The subsequent small but definite mobility decrease is said probably to be due to secondary adsorption of sodium ions. Possible explanation for the subsequent sharp mobility increase at the critical concentration is an increasing proportion of sodium ions becoming associated as gegenions with the ionic micelles.

Ekwall and Lindblad [8] demonstrated that soaps form anions with increasing valencies as the concentration increases:

Na laurate ($M \times 10^{-2}$)	Charges of laurate anion	Multivalent ion
0– 6*	1	L·HL
6–21	2	NaL·HL
21–28†	4	3NaL·HL
28–37	6	5NaL·HL

* 1–1 electrolyte.
† cmc.

As adsorption of ions by the fixed part of the double layer enormously influences zeta potential, the effectiveness of the ions increases greatly with valency increase [2]. Consequently, the valency effect of the laurate anion reaches a maximum just past the critical concentration, helping to explain the increase in mobility just past cmc and to account for the more or less gradual decline in mobility with increased concentration once the maximum has been attained.

Powney and Wood [26], in determining the protective action of soaps in maintaining in suspension particles of ilmenite black, developed the following data:

Soap	Optimum protective action ($M \times 10^{-2}$)	cmc ($M \times 10^{-2}$)
Na laurate	5	ca. 30
Na stearate	0.13	ca. 0.6
Na oleate	0.5	ca. 0.1

These would seem to indicate, for sodium laurate at least, that protective action and a single charge as

the 1-1 electrolyte is desirable. A similar deduction might fit the case of sodium stearate, but sodium oleate fails to qualify. The decrease in the suspension isotherm following the maximum for most surfactants coincides with decreased mobility, increased adsorption by the particle of long chain ion (and associated gegenion), and with increased valency of the long chain anion.

The controlling principles of critical micelle formation were reviewed to determine the degree of correlation existing between them and mobility.

1. Increase in temperature increases both cmc and mobility.

2. Added electrolytes reduce cmc (make surfactants more effective at lower concentrations) and, when used in low enough concentrations, increase mobility. Beyond a maximum concentration, further additions reduce mobility.

3. Electrolyte anions have no influence on the aggregation of anionic soaps, but they influence a positive increase in zeta potential.

4. Both cmc and zeta potential respond similarly to the Schulze-Hardy rule: the higher the valency of the cation, the less the amount required to reduce cmc and the more rapid the change toward less negative zeta potentials.

5. Mixtures of soaps have cmc values intermediate between those of the constituents but show no essential differences in zeta potential.

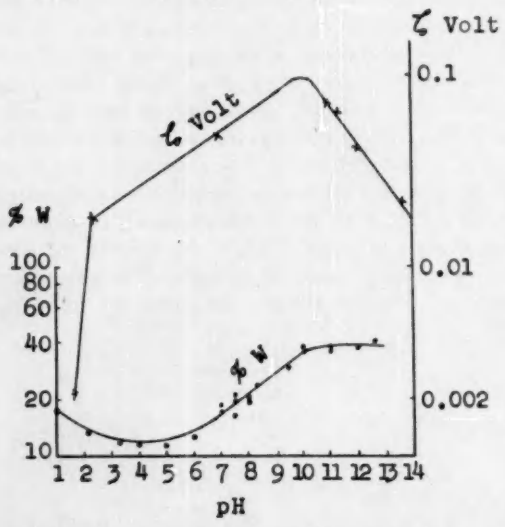

Fig. 14. Zeta potential and whiteness [11]. Zeta potentials in unbuffered solution. % W is whiteness of soiled fabric washed in buffered solutions.

Adam [2] pointed out that, for a series of aromatic sulfonic acids, the introduction of an aliphatic side chain decreased the concentration necessary to diminish zeta potential by a given amount, by a factor of 3 for each additional CH_2 group in the side chain (a case of Traube's rule in adsorption). This change in zeta potential with decreased concentration of surfactant with increased carbon chain length is related to cmc, with the exception that cmc is reduced by one-half for each increase in CH_2 in the effective carbon chain length.

Micelles themselves exhibit pronounced mobilities [35], the zeta potential of sodium lauryl sulfate being 65–100 mv. (toward the anode), with mobilities of 4.39 μ/sec./volt/cm. at 0.75% concentration (somewhat above cmc) to 3.7–3.75μ in 3.5% solutions. For micelles of surfactants, the zeta potential is that potential in water just outside the micelle with its adherent gegenions [2] which considerably affect motion in an electric field. Mobility is decreased in water from a value of 4.65 to 3.4 by adding 0.1 *M* sodium chloride. It is conceivable that at the cmc and coexistent in the solutions (and very possibly affecting the magnitude of the particle mobility) are micelles of the surfactant; these exist at one level of mobility and the particles under measurement at yet another level, the apparent particle mobility then being the resultant of its own mobility as affected by the mobility of the surfactant micelles. However, if long chain ions are adsorbed on the particle surface closely enough to move with it, the zeta potential then becomes that at the boundary of the adsorbed layer of ions [2], and the particle-adsorbed long chain ion system should have a characteristic zeta potential.

Detergency Values

Goette [11] has strongly advocated the importance of zeta potential in its effect on detergency. Figure 14 is taken from his work; the curves give a comparison of cleaning values in soapless buffer solutions, with zeta potentials of unbuffered solutions of HCl and NaOH over the pH scale. It is apparent that cleaning effectiveness and zeta potential run somewhat parallel, the optima for both lying at near pH 10–11. He did not expect complete agreement, because of the incompleteness of the data and because buffer solutions also affect mobility.

An explanation for cleaning action of alkyl sulfates in acid solutions is that the positively charged H^+ ions are displaced by long chain anions. Goette further compared the cleaning action of solutions of 0.01 *M* $K_4Fe(CN)_6$, KCl, $BaCl_2$, and $AlCl_3$ with the buffer solutions shown in Figure 8, and at the same pH: $K_4Fe(CN)_6$ cleans better because of $Fe(CN)_6^{-4}$ ion adsorption; KCl gave no change; $BaCl_2$ cleaned less well; and $AlCl_3$ gave lower cleaning, the latter two in order of their increasing cation valence.

Valence of anion in cleaning seems quite important, and Goette mentions the effective behavior of sodium hexametaphosphate and sodium pyrophosphate in preventing deposition of ilmenite black particles in concentrations as low as 5–10 ppm. The implication here is that in contrast to the sodium ion effect from Na_2CO_3 or NaOH which decrease suspension values (past a maximum value), the polyvalent anions of the complex phosphates provide protective action, possibly by preferential sorption on the electrical double layer. This assumption parallels that for the effect of increased valency of sodium laurate cited above, but data are lacking.

Stubblebine [37] correlated his mobility data with practical detergency tests, and those combinations of soap and alkali giving the most nearly equal mobilities, at the highest mobility levels, proved the best detergent mixtures. The concentration of soap (0.2%) which provided optimum soil removal also gave mobility values at the desired level (see Table II).

Systematic comparison of systems of identical materials for both zeta potential measurement and detergency and other surfactancy measurements are almost completely lacking. It must be concluded that although a direct correlation between zeta potential and detergency seems to exist, exact proof is lacking.

Summary of Factors Affecting Mobility and Zeta Potential

General

Zeta potential is the difference in potential between the immovable layer attached to the surface of a solid phase and the movable part of the diffuse layer in the body of the liquid. Though electrophoretic velocity (or mobility) generally is proportional to zeta potential, the effect of viscosity on the system must be considered. Velocity of migration of colloidal particles is independent of size, but affected, for given applied EMF, primarily by the charge density and thickness of the double layer. With water as the continuous medium, zeta potential of particles is generally negative, resulting from the dielectric character of water and the adsorbed layer of oriented water molecules which attract anions to cause an adsorption potential. The zeta potentials of particles are radically affected by treatment (or condition) prior to measurement. Temperature increase increases particle velocity.

Electrolytes

Alkaline electrolytes are more effective in increasing mobility than more neutral electrolytes. At low electrolyte concentrations, zeta potential is nearly independent of the log of concentration, but at higher concentrations a linear relationship has been found. Anions make particles negative and cations make them more positive. The greater the valency of anions and cations, the greater the effect on zeta potential (Schulze-Hardy rule and Hofmeister series).

Surfactants

Surfactants generally affect zeta potential more markedly at the maximum than do simple electrolytes. Anionic surfactants increase negative zeta potential, effect increasing with increase in effective carbon chain length up to an optimum. Cationic surfactants decrease negative zeta potential, and in sufficient concentration can change the sign of the charge. Nonionic surfactants exhibit a slight cationic effect on zeta potential.

Correlations

A clear correlation between particle suspension values and zeta potential exists: optimum suspendability and maximum zeta potential occur at nearly the same suspension agent concentrations.

Many of the generalizations covering critical micelle concentration values are related to zeta potential and mobility values; similar effects are produced by temperature change, electrolyte addition, and cation valency. Anions have no influence on aggregation of anionic soap, but influence an increase in negative zeta potential. Mixtures of soaps have cmc values intermediate between the pure materials, but show no such effect on zeta potential.

Correlation of zeta potentials with detergency values seems to exist, but definitive data are lacking.

Though excellent data are available, an increased

volume of systematic data is needed for correlation with other physico-chemical measurements made on well controlled systems.

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Moments of Distributions and Their Interrelation

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Abstract

In the field of textile research and processing, variability, both of raw material and of measurements, is unavoidable. It is explicitly implied, therefore, that analysis of data should involve an accounting of the variability and should include considerable information concerning the forms of the distribution encountered.

In such a presentation, a knowledge of distribution relationships and interrelationships is of paramount importance. The purpose of this paper is to summarize the relationships between the first few moments of several of the more common types of distributions and to point out a few applications in the analysis of data.

Specific problems are in two general categories. First, related distributions, particularly those related by a power of the variable, as with number vs. length-biased distributions, will be considered. Second, several problems regarding the sampling of mixed distributions are included. The latter deal with samples from the strata which will comprise the blend or from the blend itself. In each of these situations the effect of single and of bulk samples is treated separately.

Finally, some methods of establishing the forms of the distribution are noted for the use of those fortunate enough to be dealing with relatively large numbers of statistics.

Introduction

Moments of continuous and discrete distributions are important in studying information describing an experiment or set of experiments. Variability of a raw material or lack of precision in measurement, or both, will be involved.

The first four moments of a distribution are generally understood to represent, respectively, the mean taken about zero, the variance, the skewness, and the kurtosis, measured about the mean. Symbolically, skewness is well known; kurtosis is a symmetrical distortion from the normal (Gaussian) distribution resulting in a low center and high ends of the probability density function or, less frequently, the reverse.

The purpose of this paper is to summarize the relationships between the first few moments of several of the more common types of distributions and to point out a few of their applications in the analysis of data. The paper emphasizes the derivation of the relationships but lays no claim to originality of the underlying statistical concepts, except with regard to the manner in which they are summarized and applied.

The need for such a compilation is often encountered in textile research, where the raw material is usually quite variable and where certain characteristic measurements such as length distributions involve moments of fundamental and perturbed distributions, depending upon the method of measurement. In this field, sampling and blending problems, involving mixed distributions, are a day-by-day occurrence.

Representation of Moments

The moments of any distribution ([1], pp. 77 ff) around zero can be expressed as

$$\mu_r' = \text{ave } (x^r) = \sum_i x_i^r p(x_i) \qquad (1)$$

$$= \int_{-\infty}^{\infty} x^r f(x)\,dx \qquad (2)$$

where $p(x_i)$ and $f(x)$ are the *probability density functions;* the moments around the mean may be expressed as

$$\mu_r = \text{ave } [(x - \mu)^r] = \sum_i (x_i - \mu)^r p(x_i) \qquad (3)$$

$$= \int_{-\infty}^{\infty} (x - \mu)^r f(x)\,dx \qquad (4)$$

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where $\mu \equiv \mu_1'$. Equations 1 and 3 apply to discrete distributions, while Equations 2 and 4 are for continuous distributions.

A second method of obtaining moments is through the general moment-generating functions

$$M_x(\theta) = \int_{-\infty}^{\infty} e^{\theta x} f(x)dx \tag{5}$$

or

$$= \sum_i e^{\theta x_i} p(x_i) \tag{6}$$

around zero, and

$$M_{x-\mu}(\theta) = \int_{-\infty}^{\infty} e^{(x-\mu)\theta} f(x)dx = e^{-\mu\theta} Mx(\theta) \tag{7}$$

or

$$= \sum_i e^{(x_i-\mu)\theta} p(x_i) \tag{8}$$

around the mean.

A common method (Equation 1) of obtaining the individual moments involves taking the rth derivative of the integrated form of Equations 5, 6, 7, or 8 with $\theta = 0$ in the derivative. A more direct, and usually simpler method, is expansion of the integrated form of the moment-generating function, $M_x(\theta)$, in a Taylor series. Then

$$M_x(\theta) = M_x(0) + \theta \frac{\partial M_x(0)}{\partial \theta} + \frac{\theta^2}{2!} \frac{\partial^2 M_x(0)}{\partial \theta^2} + \frac{\theta^3}{3!} \frac{\partial^3 M_x(0)}{\partial \theta^3} + \cdots$$

The derivatives, or the coefficients of the $\theta^r/r!$, will therefore provide the moments, because $\mu_r' = \frac{\partial^r M_x(0)}{\partial \theta^r}$ by definition. Thus, $M_x(\theta) = 1 + \mu_1'\theta + \mu_2' \frac{\theta^2}{2!} + \cdots$. This system appears easier than successive differentiations, a procedure which becomes extremely laborious for higher moments. As with successive differentiation of $M_x(\theta)$, the expansion of $M_x(\theta)$ requires a single integration rather than one per moment desired as with Equations 1 through 4. However, in general, the expansion of the moment-generating function is easier than successive differentiation; use of the moment-generating function is highly advantageous when integration for each desired moment is a laborious procedure. The choice is a personal matter.

General Expressions of the Moments

Examination of either of the methods proposed above, particularly the first, will readily show that the interrelation between the various moments may be expressed in a distribution-free manner. If the expression for the rth moment around the mean is written as in Equation 3, and the term $(x - \mu)^r$ is expanded by the binomial theorem, one then obtains

$$\begin{aligned}\mu_r &= \int_{-\infty}^{\infty} (x - \mu)^r f(x)dx \\ &= \int_{-\infty}^{\infty} \Big[x^r + (-1)^1 \binom{r}{1} x^{r-1}\mu \\ &\qquad + (-1)^2 \binom{r}{2} x^{r-2}\mu^2 + \cdots \\ &\qquad \cdots + (-1)^{r-1} \binom{r}{1} x\mu^{r-1} \\ &\qquad + (-1)^r \binom{r}{0} \mu^r \Big] f(x)dx \\ &= \int_{-\infty}^{\infty} \Big[\sum_{n=0}^{n=r} (-1)^n \binom{r}{n} x^{r-n}\mu^n \Big] f(x)dx \end{aligned} \tag{9}$$

Since the integrals, $\int_{-\infty}^{\infty} x^r f(x)dx$, are the rth moments around zero, the various terms in the expansion in Equation 9 represent these various moments multiplied by numerical coefficients and by suitable powers of the mean. Therefore the general expressions for moments, valid for any distribution, can be written as follows:

$$\mu_1 = \mu_1' - \mu_1' = 0 \tag{10}$$

$$\mu_2 = \mu_2' - 2\mu_1'\mu + \mu^2 = \mu_2' - \mu^2 \tag{11}$$

$$\mu_3 = \mu_3' - 3\mu_2'\mu + 3\mu_1'\mu^2 - \mu^3 = \mu_3' - 3\mu_2'\mu + 2\mu^3 \tag{12}$$

$$\mu_4 = \mu_4' - 4\mu_3'\mu + 6\mu_2'\mu^2 - 3\mu^4 \tag{13}$$

Algebraic manipulation produces the moments about zero in terms of the moments about the mean

$$\begin{aligned}\mu_1' &= \mu \\ \mu_2' &= \mu_2 + \mu^2 \\ \mu_3' &= \mu_3 + 3\mu_2\mu + \mu^3 \\ \mu_4' &= \mu_4 + 4\mu_3\mu + 6\mu_2\mu^2 + \mu^4\end{aligned}$$

In cases where information regarding the moments of a theoretical distribution are available it is simple to go from one moment to another.

Perturbed Distributions

On occasion it is of interest to write moments of a second function $g(x)$, where $g(x)$ is related to $f(x)$

in a known manner, as for example, the following:

$$g(x) = x^r f(x)$$

With the exception noted below when $g(x)$ does not qualify as a probability density function, the procedure is simple. For example, when $r = 1$, $\nu_r' = \mu'_{r+1}/\mu$, where ν_r' represents a moment of the perturbed distribution, when $g(x)$ *can* be considered to be a probability density function. Generalizing, $\omega_r' = \mu'_{r+n}/\mu_n'$, where ω_r' represents a moment of the perturbed distribution under the same limiting condition.

In these cases, μ and μ_n' respectively are normalizing factors required to provide that the zero-th moment of the perturbed distribution shall equal unity.

Limitation. Consider the function $g(x) = \alpha x^r f(x)$. This function will be a density function only if (a) all possible values are included in the range x_1 to x_2; (b) $\alpha \int_{x_1}^{x_2} x^r f(x)dx = 1$; and (c) $x^r f(x) \geqslant 0$ between x_1 and x_2. The last condition is essential since negative values of a probability density function, by definition of probability, have no meaning.

Thus, when r is even, moments of $g(x)$ are unqualifiedly denoted by

$$\omega_r' = \mu'_{r+n}/\mu_n'$$

But when r is odd, negative values of x^r will be encountered if the range of the distribution, x_1 to x_2, includes negative values of x.

Application to Specific Distributions

The Normal Distribution

For the case of the normal distribution the probability density function is

$$f(x) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left[-1/2\left(\frac{x-\mu}{\sigma}\right)^2\right]$$

Therefore the moment-generating function may be written as

$$M_x(\theta) = \frac{1}{\sqrt{2\pi}\sigma} \int_{-\infty}^{\infty} \exp\left\{(x\theta) + \left[-1/2\left(\frac{x-\mu}{\sigma}\right)^2\right]\right\} dx$$

and the rth moment will be

$$\left.\frac{\partial^r M_x(\theta)}{\partial\theta^r}\right]_{\theta=0} = \frac{1}{\sqrt{2\pi}\sigma} \int_{-\infty}^{\infty} x^r \exp\left[-1/2\left(\frac{x-\mu}{\sigma}\right)^2\right] dx$$

Integration is simplified if it is true that

$$y = x - \mu$$

Then $x = y + \mu$, and $dx = dy$. Thus

$$\left.\partial^r M_x(\theta)/\partial\theta^r\right]_{\theta=0} = \sqrt{\frac{\alpha}{\pi}} \int_{-\infty}^{\infty} (y+\mu)^r \exp(-\alpha y^2)\, dy$$

where $\alpha = 1/2\sigma^2$. Expansion of $(y + \mu)^r$ results in the general expression

$$\mu_r' = \sqrt{\frac{\alpha}{\pi}} \int_{-\infty}^{\infty} \left[\sum_{n=0}^{n=r} \binom{r}{n} y^{r-n}\mu^n\right] \exp(-\alpha y^2)\, dy$$

Integration is readily performed if all forms of $y^k e^{-\alpha y^2} dy$ can be integrated. All the individual integral terms of this expression between $-\infty$ and $+\infty$ will be zero when k is odd; when even, the integral terms are given by

$$\frac{1 \cdot 3 \cdot 5 \cdots (k-1)}{2^{k/2}} \sqrt{\pi/\alpha^{k+1}}$$

for $k > 0$ and by $\sqrt{\pi/\alpha}$ for $k = 0$. Therefore, the first four moments of the normal distribution about zero are

$$\mu_1' = \frac{1}{\sqrt{2\pi}\sigma} \int_{-\infty}^{\infty} (y+\mu) \exp(-\alpha y^2) dy$$

$$= \frac{1}{\sqrt{2\pi}\sigma} (\mu\sqrt{2\pi}\sigma) = \mu \qquad (14)$$

and

$$\mu_2' = \frac{1}{\sqrt{2\pi}\sigma} \int_{-\infty}^{\infty} (y^2 + 2y\mu + \mu^2) \exp(-\alpha y^2) dy$$

$$= \frac{1}{\sqrt{2\pi}\sigma} (\sqrt{2\pi}\sigma^3 + \mu^2\sqrt{2\pi}\sigma) = \sigma^2 + \mu^2 \qquad (15)$$

Similarly

$$\mu_3' = 3\sigma^2\mu + \mu^3 \qquad (16)$$

and

$$\mu_4' = 3\sigma^4 + 6\mu^2\sigma^2 + \mu^4 \qquad (17)$$

From these expressions and Equations 9–13, the moments about the mean are, by algebraic manipulation,

$$\mu_1 = \mu_1' - \mu_1' = 0$$
$$\mu_2 = \sigma^2$$
$$\mu_3 = 0$$
$$\mu_4 = 3\sigma^4$$

all well-known expressions for the normal distribution.

The Normal Distribution Perturbed by a Power of the Variable

Since the normal distribution extends from $-\infty$ to $+\infty$, the limitation noted in connection with perturbed distributions applies to the moments of the normal distribution perturbed by a power of the variable. However, in the case of experimental data with general characteristics approximating normality, the subsequent remarks are a reasonable approximation if $\mu \geqslant 4\sigma$ and certainly should be acceptable when $\mu \geqslant 6\sigma$. The moments about zero of the normal distribution perturbed by a positive integral power k of the variable (as in the case of the weight, or length-biased distribution, where $k = 1$) become

$$\nu_r' = \left(\frac{\partial^r M_x(\theta)}{\partial \theta^r}\right)_{\theta=0} = \frac{1}{\sqrt{2\pi}\sigma\eta}\int_{-\infty}^{\infty} x^{k+r} \exp\left[-1/2\left(\frac{x-\mu}{\sigma}\right)^2\right] dx$$

Here ν is used in place of μ to indicate a moment of the perturbed distribution and η is a normalizing factor so that the zero-th moment will equal unity. The normalizing factor can readily be evaluated as follows:

$$\nu_0' = \frac{1}{\sqrt{2\pi}\sigma\eta}\int_{-\infty}^{\infty} x^k \exp\left[-1/2\left(\frac{x-\mu}{\sigma}\right)^2\right] dx$$

$$= \mu_k'/\eta = 1$$

$$\therefore \quad \eta = \mu_k'$$

Thus all moments of the perturbed distribution are readily calculated in terms of the original distribution. In the example, $k = 1$, with the original distribution normal,

$$\nu_1' = \mu_2'/\mu = \mu\left(1 + \frac{\sigma^2}{\mu^2}\right)$$

$$\nu_2' = \mu_3'/\mu = 3\sigma^2 + \mu^2$$

$$\nu_3' = \mu_4'/\mu = 3\sigma^4/\mu + 6\mu\sigma^2 + \mu^3$$

While there is no interest in ν_1, which must equal zero, the values ν_2 and ν_3 are generally of more interest than those of the corresponding moments about zero, and may be obtained from the latter, giving

$$\nu_2 = \sigma^2 - \left(\frac{\sigma^2}{\mu}\right)^2$$

and

$$\nu_3 = 2\sigma^6/\mu^3$$

In cases where the weight (i.e., length-biased) distribution has been measured and the parameters μ and σ^2 of a *normal* number-distribution are to be estimated, simultaneous solution of the first and second moment expressions results in the quadratic solution for μ,

$$\mu = \frac{3\nu \pm \sqrt{\nu^2 - 8\nu_2}}{4}$$

Since $\sqrt{\nu^2 - 8\nu_2}$ can be shown to be $\mu - 3\frac{\sigma^2}{\mu}$, the equation holds only when the higher root is extracted.

Having obtained μ, one can easily calculate σ^2 from the expression for ν_1'.

The Poisson Distribution

In contrast to the normal distribution, the Poisson is for a discontinuous, or discrete, distribution. Therefore $f(x)$ is more correctly written as $p(x_i)$, with

$$p(x_i) = e^{-\lambda}\lambda^{x_i}/x_i!$$

where λ is the mean number of successes and x_i is the number of successes in N trials. The moment-generating function is then correctly written as

$$M_x(\theta) = \sum_0^{\infty} e^{\theta x_i} p(x_i)$$

and values of the moments are obtained in the usual manner. As previously noted, the rth moment is derived from the rth partial derivative with respect to θ, with $\theta = 0$. Therefore

$$\mu_r' = \sum_0^{\infty} (x^r e^{-\lambda}\lambda^x/x!)$$

This form can be readily handled through β-functions or simply through the knowledge that the zero-th moment must equal unity, representing the summation of all the possibilities of occurrence of x successes for all possible values of x. Thus

$$\sum_0^{\infty} (e^{-\lambda}\lambda^x/x!) = 1$$

and it follows that the same is true for any other power of λ, when this power is the same as the factorial term in the denominator. It is therefore simple to derive the moments by rewriting x^r

as $x(x-1)\cdots(x-r+1)$ with the proper residual terms added. For example, where $r=2$ and $r=3$,

$$x^2 = x^2 - x + x = x(x-1) + x$$
$$x^3 = x(x-1)(x-2) + 3x(x-1) + x$$

The summation may now be treated as follows:

$$\mu_1' = \sum_0^\infty (xe^{-\lambda}\lambda^x/x!) = \lambda \sum_0^\infty e^{-\lambda}\lambda^{x-1}/(x-1)! = \lambda$$

$$\mu_2' = \sum_0^\infty (x^2 e^{-\lambda}\lambda^x/x!)$$

$$= \sum_0^\infty x(x-1)e^{-\lambda}\lambda^x/x! + \sum_0^\infty (xe^{-\lambda}\lambda^x/x!)$$

$$= \lambda^2 \sum_0^\infty [e^{-\lambda}\lambda^{x-2}/(x-2)!] + \lambda$$

$$= \lambda^2 + \lambda$$

Similarly, it can be shown that

$$\mu_3' = \lambda^3 + 3\lambda^2 + \lambda$$

and

$$\mu_4' = \lambda^4 + 6\lambda^3 + 7\lambda^2 + \lambda$$

Transforming these moments-about-zero to moments-about-the-mean in the usual manner, using Equations 9, 10, and 11,

$$\mu_1' = \lambda$$
$$\mu_2 = \lambda$$
$$\mu_3 = \lambda$$

and

$$\mu_4 = \lambda + 3\lambda^2$$

Also in the manner discussed for the normal distribution

$$\nu_1' = \mu_2'/\mu = \lambda + 1 = \nu$$

and

$$\nu_2' = \mu_3'/\mu = \lambda^2 + 3\lambda + 1$$

From the last expressions and Equation 9, $\nu_2 = \lambda$, indicating that while the mean of the perturbed distribution is shifted to the right, the variance is unchanged, an important property of the Poisson distribution.

The Uniform (Square) Distribution

For the case where no values of x occur below a lower limit, L_1, or above an upper limit, L_2, and where the frequency of all values between these limits is a constant, the distribution is uniform, or square. The zero-th moment indicates that the constant, $f(x)$, is a function of the range, $L_2 - L_1$. Since

$$\int_{L_1}^{L_2} f(x)dx = 1$$

$$f(x)(L_2 - L_1) = 1$$

and

$$f(x) = \frac{1}{L_2 - L_1}$$

for $L_1 \leqslant x \leqslant L_2$ and

$$f(x) = 0$$

for $L_1 > x > L_2$. As expected, the probability of a value of x in the range $L_1 \leqslant x \leqslant L_2$ increases as the range decreases.

All moments can be written in terms of the limiting values, and all moments about the mean will be expressible in terms of the range.

$$\mu_1' = \int_{L_1}^{L_2} xf(x)dx = \frac{(L_2^2 - L_1^2)}{2(L_2 - L_1)} = (L_2 + L_1)/2$$

$$\mu_2' = \int_{L_1}^{L_2} x^2 f(x)dx = (L_2^2 + L_2L_1 + L_1^2)/3$$

$$\mu_3' = (L_2^3 + L_2^2L_1 + L_2L_1^2 + L_1^3)/4$$

$$\mu_4' = (L_2^4 + L_2^3L_1 + L_2^2L_1^2 + L_2L_1^3 + L_1^4)/5$$

The moments about the mean then become

$$\mu_1 = 0$$
$$\mu_2 = (L_2 - L_1)^2/12$$
$$\mu_3 = 0 \text{ (the distribution is symmetrical about } \mu)$$
$$\mu_4 = (L_2 - L_1)^4/80$$

In the case of the normal distribution, $\mu_4 - 3\mu_2^2$, a quantity known as the fourth cumulant (or semi-invariant), will equal zero. However, for the square distribution, a negative value is obtained.

$$\kappa_4 = \mu_4 - 3\mu_2^2 = -(L_2 - L_1)^4/120$$

Negative values of the fourth cumulant for a bell-shaped distribution indicate an excess of values around the mean and a deficiency of extreme values. However, it can be seen that exactly the opposite is true with the square distribution, where no values exist in the real extremes of the x-axis. Obviously, extremes contribute heavily to fourth moments and consequently to the fourth cumulant.

It can be readily shown that the maximum ordi-

nate of a normal distribution with unit value of the zero-th moment and $\mu_2 = (L_2 - L_1)^2/12$ (corresponding to μ_2 for the square distribution) bears a constant ratio of $\sqrt{6/\pi}$ to the single value of the ordinate of the square distribution. Further, 8.33% of the values of the normal distribution lie above L_2 and below L_1, emphasizing the sparsity of extreme values in the uniform distribution as noted above. It should be further noted, however, that the absolute value of κ_4 increases as the range increases, since the greater absolute values of the extremes of the corresponding normal distribution contribute more heavily to the zero value of the cumulant in this case. For example,

L_1	L_2	κ_4
a	$3a$	$-0.1333\,a^4$
0	$2a$	$-0.1333\,a^4$
0	$4a$	$-2.1333\,a^4$
a	$5a$	$-2.1333\,a^4$

If, for the square distribution, there are no negative values of x, moments of the distribution perturbed by the first power of the variable are simply derived. The first two are:

$$\nu_1' = \frac{2(L_2^2 + L_2L_1 + L_1^2)}{3(L_2 + L_1)}$$

and

$$\nu_2' = \frac{L_2^4 + 2L_2^3L_1 - 6L_2^2L_1^2 + 2L_2L_1^3 + L_1^4}{18(L_2 + L_1)^2}$$

Values of moments for a series of representative square distributions are listed below.

	$0 \leqslant x \leqslant 2a$	$a \leqslant x \leqslant 3a$	$0 \leqslant x \leqslant 4a$	$a \leqslant x \leqslant 5a$
μ	a	$2a$	$2a$	$3a$
μ_2'	$4a^2/3$	$13a^2/3$	$16a^2/3$	$31a^2/3$
μ_2	$a^2/3$	$a^2/3$	$4a^2/3$	$4a^2/3$
μ_3'	$2a^3$	$10a^3$	$16a^3$	$39a^3$
ν	$4a/3$	$13a/6$	$8a/3$	$31a/9$
ν_2'	$2a^2$	$5a^2$	$8a^2$	$39a^2/3$
ν_2	$2a^2/9$	$11a^2/36$	$8a^2/9$	$92a^2/81$

The Moment-Generating Function

If the moment-generating function is analytic and is defined as

$$M_x(\theta) = \int_{-\infty}^{\infty} e^{\theta x} f(x)\,dx$$

it may be expanded in a Taylor series

$$M_x(\theta) = M_x(0) + \theta \frac{\partial M_x(0)}{\partial \theta} + \frac{\theta^2}{2!} \frac{\partial^2 M_x(0)}{\partial \theta^2} + \cdots$$

and the differential coefficients of $\theta^n/n!$ are seen to be the required moments. The Taylor series expansion can be used to determine the moments in a much simpler fashion than by successive differentiation of the integral form. The square, normal, and Poisson distributions will be used to illustrate the ease of finding moments by applying the Taylor series method.

Square distribution:

$$M_x(\theta) = \frac{1}{2a} \int_a^{3a} e^{\theta x} dx = \frac{e^{3a\theta} - e^{a\theta}}{2a\theta}$$

$$\therefore M_x(\theta) = \left[1 + 3a\theta + 9a^2 \frac{\theta^2}{2!} + 27a^3 \frac{\theta^3}{3!} + 81a^4 \frac{\theta^4}{4!} + \cdots - 1 - a\theta - a^2 \frac{\theta^2}{2!} - a^3 \frac{\theta^3}{3!} - a^4 \frac{\theta^4}{4!} - \cdots\right] \Big/ 2a\theta$$

$$= 1 + (2a)\theta + \frac{13a^2}{3} \frac{\theta^2}{2!} + 10a^3 \frac{\theta^3}{3!} + \cdots$$

Normal distribution:

$$M_x(\theta) = \frac{1}{\sqrt{2\pi}\sigma} \int_{-\infty}^{\infty} e^{\theta x} e^{-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2} dx$$

The integrand may be written as

$$\exp\left(\mu\theta + \frac{\sigma^2\theta^2}{2}\right) e^{-\frac{1}{2}\left(\frac{x-\mu-\sigma^2\theta}{\sigma}\right)^2} d\left(\frac{x - \mu - \sigma^2\theta}{\sigma}\right)$$

which is of the form

$$\exp\left(\mu\theta + \frac{\sigma^2\theta^2}{2}\right) \int_{-\infty}^{\infty} e^{-\frac{1}{2}y^2} dy$$

The last integral has been shown previously to be equal to $\sqrt{2\pi}\sigma$. Therefore

$$M_x(\theta) = \exp\left(\mu\theta + \frac{\sigma^2\theta^2}{2}\right)$$

$$= 1 + \left(\mu\theta + \frac{\sigma^2\theta^2}{2}\right) + \left(\mu^2\theta^2 + \mu\sigma^2\theta^2 + \frac{\sigma^4\theta^4}{4}\right)/2! + (\mu^3\theta^3 + \tfrac{3}{2}\mu^2\theta^4\sigma^2 + \tfrac{3}{4}\mu\theta^5\sigma^4 + \tfrac{1}{8}\sigma^6\theta^6)/3! + (\mu^4\theta^4 + \cdots)/4! + \cdots$$

$$= 1 + (\mu\theta) + (\mu + \sigma^2) \frac{\theta^2}{2!} + (\mu^3 + 3\mu\sigma^2) \frac{\theta^3}{3!} + (\mu^4 + 6\mu^2\sigma^2 + 3\sigma^4) \frac{\theta^4}{4!} + \cdots$$

The individual coefficients of $\frac{\theta^r}{r!}$ are the rth moments and may be checked against the distribution-free expressions for the first four as given in Equations 14 through 17.

Poisson distribution:

In this case the moment-generating function may be shown [1] to be

$$M_x(\theta) = e^{\lambda(e^\theta - 1)}$$

Expansion of the exponential gives

$$M_x(\theta) = 1 + \lambda(e^\theta - 1) + \frac{\lambda^2(e^\theta - 1)^2}{2!} + \cdots$$

Further expansion of the remaining exponential terms and simplification yields

$$M_x(\theta) = 1 + \lambda\theta + (\lambda + \lambda^2)\frac{\theta^2}{2!} + (\lambda^3 + 3\lambda^2 + \lambda)\frac{\theta^3}{3!} + \cdots$$

with coefficients of $\frac{\theta^r}{r!}$ providing moments for this distribution in agreement with those derived in the preceding section.

It is readily apparent that this method includes one integration plus simple algebra in place of the single integration per moment required by the method of partial differentiation of $M_x(\theta)$ prior to integration. Although the preference is a personal matter, the neatness of the immediately preceding method is appealing.

Practical Applications

Four applications will be briefly considered: (a) estimation of distribution parameters for $f(x)$ from data on the distribution $xf(x)$; (b) effect of moments of the $f(x)$ distribution on the estimate of the mean of the $x^r f(x)$ distribution; (c) estimation of parameters of mixtures from distributions of known parameters; and (d) estimation of distribution type.

The first is a common problem in textile fiber testing: the desirability of estimating number distribution parameters when a weight distribution (e.g., Suter-Webb sort) has been used experimentally, or vice versa. The second problem can be illustrated by the effect upon bending stiffness of variance in the number distribution for samples of the same mean diameter. The third is fundamental to blending, and the last is important in any case where violation of the assumptions of a statistical test may affect tabular significance levels.

Parameter Transformations

Assume that number-length-distribution data are available for a set of fibers. Since

$$\nu_r' = \mu'_{r+1}/\mu$$

the desired length-biased mean, ν, and length-biased variance, ν_2, may be calculated from

$$\nu_2' = \mu_3'/\mu$$

and

$$\nu = \mu_2'/\mu$$

since

$$\nu_2 = \nu_2' - \nu^2$$

These two will be true regardless of the form of the number distribution. However, the problem is simplified when it can be assumed that the number distribution is normal, or even symmetrical. Then $\mu_3 = 0$ and Equations 14 and 15 apply.

To illustrate these moment interrelationships, data have been chosen from various samples of wool studied in the Textile Research Institute Wool Research Project [5]. The *number distributions* were obtained on the TRI length tester [8]; these data were also used to calculate the length-biased distributions. The latter are equivalent to weight distributions if constant mass per unit length is a good assumption.

The length-biased parameters, ν and ν_2, were calculated first assuming that the number distributions were normal; subsequently these parameters were recalculated without this assumption.

These data are summarized in Table I.

In general the means and standard deviations predicted through use of μ_1 and μ_2 are in good agreement with those calculated from the length data despite apparent low ratios of μ/σ. When the third moment is added, agreement should be perfect, and no discrepancies are found in the means. The slight discrepancies in the standard deviations are due to using grouped data instead of dealing with each fiber individually and, more important, due to use of the moments, as calculated from the data estimates, rather than the true parameters of the distributions.

The third moments are all significantly different from zero ($\alpha = 5\%$ for Wool 2 and 1% for the other three). Samples 1 and 3 are fibers taken from

greasy wool, while 2 and 4 are taken from tops. The skewness of the greasy wool samples is negative, indicating more short fibers than in a symmetrical distribution; the positive skewness of the top samples is characteristic of samples from a process in which short fibers are preferentially removed. It is interesting to speculate on the magnitude of the third moment as an evaluation of the comber efficiency.

Since a comb sorter is a common tool in textile work, it is useful to be able to estimate the mean and the standard deviation of the number distribution from the moments of the length-biased distribution. As previously noted,

$$\nu_2' = \frac{\mu_3'}{\mu}$$

$$\nu = \nu_1' = \frac{\mu_2'}{\mu}$$

and

$$\sigma^2 = \mu_2' - \mu^2$$

If one assumes that the number distribution is normal, and ignores the limitations of perturbed normal distributions previously noted, only the first and second moments of the length-biased distribution are needed. As this calculation is based on the "calculated" values of Wool 2, μ is estimated to be 2.79 and σ is estimated to be 1.283. As expected, the agreement, while good, is not perfect. No attempt has been made to make this calculation without assuming $\mu_3 = 0$; it is possible to make the calculations, but the solutions are much more difficult and little gain over complete recalculation of the data would be obtained.

Bending Stiffness

The bending stiffness of a fiber can be shown [6] to be proportional to the fourth moment of the number distribution of radii and may therefore be written in the form

$$k_B = a(3\sigma^4 + 6\sigma^2\mu^2 + \mu^4)$$

when the radii are normally distributed. Thus if two samples of fibers have the same mean radius, μ, but differ in their variances, σ_1^2 and σ_2^2, it is apparent that the bending stiffnesses will be different and their ratio a function of the variances. In an actual case these conditions existed, the estimated mean diameters of 23.22 and 23.47 microns being identical within the error of measurements, while the standard deviations were quite different, being estimated as 5.53 and 3.99 microns. Since a is a constant, the ratio of the bending stiffness of one sample to that of the other is calculated to be 1.12, while the value is found to be 1.14, an excellent agreement.

Since the expression for bending moment includes both μ and σ, the equality of the means of the two samples which occurred in the example is not a prerequisite to calculation of the expected value of the ratio. Normality of the distribution of the radii is equally unessential. The simplifications for the normal distribution, $\mu_4 = 3\sigma^2$ and $\mu_3 = 0$, no longer apply, and

$$k_B = a(\mu_4 + 4\mu_3\mu + 6\sigma^2\mu^2 + \mu^4)$$

Both third and fourth moments must be estimated from the data if the ratio of k_B for two non-normal samples is to be calculated. Moreover, the failure of the sample to represent perfectly the population will be much more serious when higher moments are involved. The number of fibers in each sample should therefore be very large, preferably $N \geqslant 500$, when severe non-normalities are encountered.

Mixed Populations

For the case of several populations, with no specified density form, to be mixed in fractions f_i of each, the probability density function of the mixture is

$$\phi(x) = f_1\phi_1(x) + f_2\phi_2(x) + \cdots + f_k\phi_k(x)$$

$$= \sum_{i=1}^{k} f_i\phi_i(x)$$

The moments of the mixed population are

$$\mu_r' = \int_{-\infty}^{\infty} x^r\phi(x)dx = \int_{-\infty}^{\infty} x^r[\sum_i f_i\phi_i(x)]dx$$

$$= \sum_i f_i\mu_{ir}'$$

The first two moments, which are those most frequently required, are

$$\mu_1' = \sum_i f_i\mu_i = \mu$$

and

$$\mu_2' = \sum_i f_i\mu_{i2}'$$

The latter is more valuable when evaluated about the mean, where

$$\mu_2 = \mu_2' - \mu^2$$

Therefore

$$\mu_2 = \sum_i f_i(\mu_{2i} + \mu_i^2) - \mu^2$$

TABLE I

Wool sample	Number distribution $\hat{\mu}_1$ (=$\hat{\mu}$)	Number distribution $\sqrt{\hat{\mu}_2}$ (=$\hat{\sigma}$)	Number distribution $\hat{\mu}_3$	Length-biased distributions* Estimates obtained by calculation: Number distribution $\hat{\nu}$	Number distribution $\sqrt{\hat{\nu}_2}$	μ_1, μ_2 only $\hat{\nu}$	μ_1, μ_2 only $\sqrt{\hat{\nu}_2}$	μ_1, μ_2, μ_3 $\hat{\nu}$	μ_1, μ_2, μ_3 $\sqrt{\hat{\nu}_2}$
1	4.35	1.000	−1.1488	4.64	0.844	4.58	0.975	4.64	0.856
2	2.83	1.279	0.4006	3.38	1.141	3.41	1.141	3.38	1.141
3	5.33	0.970	−1.0040	5.56	0.873	5.50	0.954	5.56	0.903
4	2.79	1.450	1.6326	3.58	1.450	3.54	1.250	3.58	1.459

* To avoid confusion and to be consistent with previous nomenclature, the mean is denoted as ν and the standard deviation as $\sqrt{\nu_2}$.

Thus

$$\mu_2 = \sum_i f_i\mu_{2i} + \sum_i f_i\mu_i^2 - \mu^2$$

or

$$= \sum_i f_i\sigma_i^2 + \sum_i f_i\mu_i^2 - \mu^2$$

where σ_i^2 is the variance within the ith original population. Moreover, since $\sum_i f_i\mu_i^2$ is a second moment about zero, the last two terms are a second moment for the population means around the new grand mean of the mix.

When $f_1 = f_2 = \cdots = f_k$, and $\sigma_1 = \sigma_2 = \cdots = \sigma_k$, the expression reduces to

$$\mu_2 = \sigma^2 + \sigma_{\mu_i}^2$$

as would be expected. When the f's are not equal the summations must be retained for proper weighting of the fractions mixed.

Many potential pitfalls threaten interpretations drawn from a casual application of statistical formulae to problems of blending. The moments of the mixed distribution do not tell the whole story, as anyone familiar with analysis of variance would readily conclude. However, additional information obtainable from analysis of variance is still insufficient for a complete picture.

Two major categories of problems will be treated, each with attendant special cases. The line of demarcation is drawn in relation to the method of evaluating the desired property and the consequent type of sample drawn—individual units or bulk. Characteristic of the former is a single fiber, as for a length or diameter measurement; the latter, as implied, involves a mass, as with the Micronaire for fineness.

Individual Samples

With individual fibers, the moments of the mixture are particularly applicable. If the sample units are randomly drawn, no questions of perfection of blending are involved.

However impractical the blend may be, consider a mixture of the four wools previously summarized, using the number distributions.

$$\hat{\mu}_{11}' = 4.35 \qquad \hat{\sigma}_1^2 = 1.0000$$
$$\hat{\mu}_{12}' = 2.83 \qquad \hat{\sigma}_2^2 = 1.6358$$
$$\hat{\mu}_{13}' = 5.33 \qquad \hat{\sigma}_3^2 = 0.9409$$
$$\hat{\mu}_{14}' = 2.79 \qquad \hat{\sigma}_4^2 = 2.1025$$
$$\sum\sigma_i^2 = 5.6792$$

If the four are blended in equal proportions ($f_1 = f_2 = f_3 = f_4 = \frac{1}{4}$), $\hat{\mu}_1 = 3.825$, and

$$\hat{\mu}_2 = 1.4198 + \frac{(4.35)^2}{4} + \cdots + \frac{(2.79)^2}{4} - (3.825)^2$$
$$= 1.4198 + 1.1504 = 2.5702$$

However, if one is interested only in predicting the mean of the blend, and the precision of its estimate, one may consider that this is a case of *stratified sampling* (see any standard text, as for example [7], pp. 504–507, [1], pp. 61–65, or [3], pp. 345–346). Then the variance between means is not involved, due to the stratified condition of the sampling. With equal fractions the mean, $\bar{x}$, is obtained as before, and

$$\text{var}\,(\bar{x}) = \sum_{i=1}^{4}\left(\frac{1}{4}\right)^2\frac{\sigma_i^2}{N_i} = \frac{1}{16}\sum\frac{\sigma_i^2}{N_i}$$

where N_i is the number of randomly selected fibers sampled in the ith wool. If the N_i are equal, the variance of the estimated mean is

$$\frac{5.6792}{16N} = \frac{0.3544}{N}$$

The estimate may be made as precise as desired by choice of N.

Compare 400 fibers randomly chosen from the blend with 100 each from the four strata:

	Var. ($\bar{x}$)
Stratified sampling	0.0035
Blend sampling, $\mu_2 = \sigma^2 + \sigma_\mu^2$	0.0064

A further problem remains: the precision of a mean estimate with the component parts drawn at random from p populations where the variances within and between populations are known or have been estimated by an experimental program. This is the familiar problem of the use of components from the analysis of variance. As an example, suppose that the four wools were drawn at random from a large number of wools any of which might be used in the final blend. Then $\hat{\sigma}_E^2 = 1.4198$ and $\hat{\sigma}_E^2 + 100\,\hat{\sigma}_w^2 = 115.04$, where $\hat{\sigma}_w^2$ is the component of between-wools variance; therefore, $\hat{\sigma}_w^2 = 1.1362$. A representative problem might be the variance of the estimated blend mean when N fibers are taken from each of k wools.

$$\text{var}\,(\bar{x}) = \frac{\sigma_E^2}{Nk} + \frac{\sigma_w^2}{k}$$

Not only the variance but the most economical sampling procedure could be determined in this case if the cost of measurements and sample selection were both known (e.g., [7], pp. 515–519).

Bulk Samples

The previous remarks are essentially standard. The less-known pitfalls would seem to occur with bulk samples. Here, for example, with perfect blending and perfect sampling, the variance between component elements of the blend does not appear, a fact that is not always immediately apparent.

To treat this case somewhat more extensively, consider first sampling the elements (e.g., cotton bales) which are to compose the blend and, second, consider samples from the blend.

Elements. The elements which comprise the blend may each be sampled, resulting in a system of stratified sampling. Or, a representative group may be studied and the expected variance of the mean may be estimated. To illustrate these cases, take the data of Brenner and Scocca [2], Table I, dealing with Micronaire readings on 16 bales of cotton from a single regional source. From the data $\hat{\sigma}_E^2 = 0.0193$ (175 df) and appears to be thoroughly homogeneous, bale-to-bale, in terms of a Bartlett test; further, σ_c^2 can be estimated to be 0.1384; σ_c^2 is the component due to between-cottons variance.

If k specific bales from this group are to be blended, the mean can be estimated as the average of the individual bales (4.628 when $k = 16$, or 4.595 when bales 1, 2, $\cdots$ 5 only are included) and the variance of this average is σ_E^2/kN, where $\sigma_E^2 = 0.0193$, N is samples per bale, and k is the number of bales.

However, if some general group of bales from this variety and growing area are to be blended, the mean will be estimated as before, but the variance is then

$$\frac{\sigma_E^2}{kN} + \frac{\sigma_c^2}{k}$$

where k is the number of bales randomly chosen for analysis.

Blends. If the blend is to be sampled, instead of the elements (i.e., the bales) from which it is composed, the variance may be represented as $\sigma_E^2 + C\sigma_c^2$, where $0 \geqslant C \geqslant 1$.

The exact value of the constant C depends upon the perfection of blending attained before sampling. With a perfect blend and a sample perfectly representative of the blend, there is no sample-to-sample variability, so that $C = 0$. With no blending, so that each sample is drawn completely and randomly from one of the component elements, $C = 1$. The usual case would be intermediate, but C is then unknown and constitutes some measure of perfection of blend.

Suppose that a blend is desired from several bales of cotton of the same source and variety discussed by Brenner and Scocca. If both blend and samples are perfect, the mean value of the blend can be estimated by the average of the N samples analyzed. The variance of this average is estimated to be $0.0193/N$.

However, if the samples were taken at such a point in processing, or in such a manner as to come from unmixed layers, the variance of the average would be $(0.0193 + 0.1384)/N = 0.1577/N$. This latter value would also apply if the samples were so small as to provide a guarantee that each sample comes from a single entering element of the blend, in this case a bale. This situation, however, is the

pure case of the mixture of distributions, described earlier.

DISTRIBUTION TYPE FROM ESTIMATES OF PARAMETERS

The character of the population from which a series of samples is drawn is frequently of interest. For example, there have been examples earlier in which normality of the number distributions was of interest. If sufficient data exist, frequency histograms can be prepared or the cumulative curve can be drawn on probability paper. General symmetry (or alternately, skewness) can be estimated qualitatively by the first; normality can be judged qualitatively by the straightness of the line in the second. In contrast, the moments of any particular distribution are quantitative, with the third and fourth about the mean being particularly interesting in this respect.

With information available only from samples rather than knowledge of the whole population, the third and fourth moments can only be estimated; various methods are suggested for testing the extent of the departure of third and fourth moment estimates from values predicted by the moments of the distribution under consideration. Usually another quantity, the cumulant, is derived from the moments, and tests for departure from prediction are made through these cumulants; this procedure is more convenient in that all cumulants of the normal distribution equal zero. Since the cumulants, denoted as $\kappa_1, \kappa_2, \cdots \kappa_n$ must be estimated, their estimates are termed the k-statistics. The test is usually made on the g-statistics, which are dimensionless and are defined as $g_1 = k_3/k_2^{3/2}$ and $g_2 = k_4/k_2^2$. The tests can now take the form of t-tests as suggested by Snedecor [7]

$$t = \frac{g_1}{s_{g_1}}$$

for skewness, where

$$s^2_{g_1} = 6n(n-1)/(n-2)(n+1)(n+3)$$

and

$$t = \frac{g_2}{s_{g_2}}$$

for kurtosis, where

$$s^2_{g_2} = 24n(n-1)^2/(n-3)(n-2)(n+3)(n+5)$$

Bennett and Franklin [1] substantially support these methods. However, they take the conservative view that the tests cannot be made satisfactorily unless the cumulants, κ, are substantially known. This level of "knowledge" requires a very large number of samples, with N in the neighborhood of 500. Under these circumstances, the variances of the g-statistics can be simplified:

$$\text{var } (g_1) \sim 6/n$$
$$\text{var } (g_2) \sim 24/n$$

Both tests involve the experimenter in the danger of multiple dependent t-tests without modification of the significance levels and are therefore dangerous. The "goodness of fit" test, with a χ^2 test of the overall suitability of the chosen distribution as a representation of the population from which the sample is drawn, is probably more sound. This test is well known and well described in many standard texts (e.g., [1, 4, 7]).

Summary

Statistical methods contribute materially to the interpretation of experimental results. As variability of raw materials or measurements increases, statistical methods become increasingly important. It is then essential that the contributions of distributional parameters in the analysis of experimental data be thoroughly understood.

For this reason, this paper has dealt extensively with the interrelation of moments in any one distribution and in mixtures of distributions. Application to fiber distributions (length and diameter), both typical textile problems, have been considered. Several problems have been included which relate to the method of sampling and to the interpretation of the estimated means.

Acknowledgment

The authors wish to take this opportunity to note their deep appreciation of the advice and suggestions received from Dr. Hale C. Sweeny, of the Atlantic Refining Company. In particular, they wish to note his contributions to the sections dealing with perturbed distributions and square distributions.

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The Significance of Wool Fiber Crimp

Part II: A Study on the Woolen System

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Introduction

The effect of wool fiber crimp on the physical and mechanical properties of fiber assemblies prepared on the French worsted system, and the changes in fiber crimp which take place in worsted processing, were discussed in Part I of this series [2]. Two Merino wools, closely matched in all their characteristics other than crimp, were used for this purpose. At the conclusion of that investigation, about 170 lb. of each wool, in the form of top, was available for further study. The top, cut to a nominal length of 2 in., formed the raw material for the work on the woolen system described below.

The background of this inquiry, the properties of the raw wools, and the experimental methods used are described in detail in Part I [2]; consequently, no extensive discussion is needed here.

Processing

The cut tops were picked, oiled and tinted, carded (using Peralta rollers), and ring-spun into a 6-run (516 grex) yarn, 19 t.p.i. The steamed singles yarn formed both warp and filling for a plain weave ladies' dress fabric, woven with 2400 threads, 68½-in. reed, 34 picks/in. The finishing routine was: dry clean; soap scour in dolly; dye, scutch, and squeeze; tenter dry; full decate; wet out in dolly; squeeze; tenter dry; shear; steam tenter frame; and semi-decate. Three shades were dyed (tan, red, and blue), level-dying acid dyes being used. One of the pairs of fabrics (tan) was given a light (10 min.) soap-fulling prior to scouring.

The thread counts and weight of the fabrics are listed in Table I.

The only observed processing difference between the two wools was in carding. The high-crimp wool carded satisfactorily; the low-crimp, under the same conditions, gave an excessive amount of fly, and it was necessary to reduce the throughput, to replace the fancy on the front of the cylinder by an open-set one, and to reduce the fancy speed to obtain acceptable performance [3].

Fiber Properties

The fiber lengths at various processing stages, determined on the TRI single-fiber tester, are listed in Table II.

The fiber tensile properties, measured at various processing stations, showed the same general trends as have been observed in the worsted study. The values for two properties, uncrimping stress and breaking stress, measured at 65% RH and 70° F., are given in Table III; the data obtained at corresponding stations on the two systems are listed side by side.

As in the worsted investigation, the uncrimping stress of the high-crimp wool decreases through yarn manufacture, that of the low-crimp remaining un-

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altered; again, there is an increase on passing into fabric, but this time, the difference between the two wools is not completely eliminated. The Young's modulus shows corresponding changes (in the reverse sense).

The drop in fiber breaking stress through the yarn stage is similar on the two processing systems, which suggests that the degree of mechanical damage is about the same in the two cases. In other words, passage through Peralta rollers does not produce a detectable modification in the fiber properties.

TABLE I. Threads and Picks Per Inch and Weight Per Unit Area

	Threads/ in.	Picks/ in.	oz./ sq. yd.
Ready to dye	42	36	5.4
Finished—Tan (fulled)	43	34	5.5
Red	41	34	5.2
Blue	41	34	5.2

TABLE II. Fiber Length (Numerical Data)

	High crimp		Low crimp	
	Mean, in.	C. V., %	Mean, in.	C. V., %
Top (before cutting)	2.83 ± 0.13	45.2	2.79 ± 0.15	52.0
Picker lot*	1.62 ± 0.10	43.2	1.90 ± 0.09	34.1
Woolen roving	1.39 ± 0.11	57.2	1.38 ± 0.10	53.3

* In view of the difficulties in sampling at this stage, these values should be regarded with caution.

The reduction in the ultimate tensile properties of the fibers from the ready-to-dye state to the finished fabric, due largely to the chemical degradation, is much smaller in the woolen fabrics, where a milder dyeing process was used. The point is illustrated by the data in Table IV, where the fiber breaking energy per unit volume, measured in borate buffer solution at pH 9.2, is listed for the various stages. In the woolen experiment, the extent of chemical attack was insufficient to reveal the greater sensitivity to damage of the low-crimp wool.

Yarn Properties

The single-strand tensile properties and yarn bulk density are reported in Table V. The former were measured on the yarn in oil, and the latter after soap scouring.

It is difficult to compare these values with the corresponding worsted data,[2] because the amount of twist employed cannot be readily equated for the two types of structure. The twist multiple used here[3] gives a fairly soft woolen yarn but a hard worsted one. Nevertheless, it may be said that the differences between the two wools observed here are surprisingly small, both in magnitude and in statistical significance, in comparison with those found in the worsted work.

A small scale investigation of the effect of twist

[2] Figures 12 and 13 of Reference [2].

[3] Metric twist constant = (turns/cm.)^2 × count in grex × 10^{-4} = 2.87.

TABLE III. Changes in Two Fiber Tensile Properties at 65% RH and 70° F. through Worsted and Woolen Processing

Stage	Worsted			Woolen		
	High crimp	Low crimp	P*	High crimp	Low crimp	P*
	Uncrimping stress, megagrams cm.$^{-2}$					
Raw wool	0.117	0.077	→0	—	—	—
Top	0.096	0.073	0.001	—	—	—
Picker lot	—	—	—	0.098	0.079	0.001
Yarn	0.085	0.076	0.01	0.080	0.075	0.05
RTD fabric	0.101	0.097	>0.2	0.093	0.085	0.01
Finished fabric, Tan†	0.101	0.103	→1	0.092	0.083	0.01
	Breaking stress, megagrams cm.$^{-2}$					
Raw wool	1.56	1.64	>0.2	—	—	—
Picker lot	—	—	—	1.53	1.64	0.2
Yarn	1.44	1.49	>0.2	1.39	1.47	0.2
RTD fabric	1.47	1.57	>0.2	1.37	1.48	0.2
Finished fabric, Tan†	1.17	1.10	>0.2	1.36	1.36	1

* The statistic P represents the probability of an effect occurring by chance.

† Chrome complex dyes of the 1 : 1 type in the case of the worsted, acid dyes in the woolen fabrics.

TABLE IV. Fiber Breaking Energy per Unit Volume (megagrams cm.$^{-2}$) in pH 9.2 Buffer, in Ready-to-Dye and Finished Fabrics

Stage	Worsted			Woolen		
	High crimp	Low crimp	*P*	High crimp	Low crimp	*P*
Ready to dye	0.293	0.308	0.1	0.303	0.306	→1
Finished—Tan*	0.157	0.136	0.05	0.230	0.238	→1
Navy*	0.212	0.188	0.2	—	—	—
Red*	—	—	—	0.274	0.266	→1

* Chrome complex dyes of the 1 : 1 type in the case of the worsted, acid dyes in the woolen fabrics.

on the tensile properties was made, on the high-crimp yarn only, by adjusting the twist content of the individual strands on a twist tester and then breaking these on the Instron tester. The results are indicated graphically, together with the data for the corresponding worsted yarns, in Figure 1. In all the three measured properties, a displacement of the woolen curves upward on the twist constant axis is evident.

Fabric Properties

Handle and Appearance

The fabrics made from the high-crimp wool were considered by experts to have a softer hand and finer appearance than their low-crimp counterparts [3]. The difference between the wools was readily detectable; however, contrary to expectation, it was not strikingly greater than that observed in the tightly set, tightly twisted worsted charmeen structure, where the effect of crimp might be expected to be minimized.

Fabric Thickness

The mean values for thickness are given in bar-graph form in Figure 2; they were determined by the procedure previously described [2] on samples relaxed by wetting and drying in the absence of tension.

The high-crimp fabrics are, on the average, about 6% thicker than the low-crimp; in the worsted materials, the difference was 10%. The greater thickness of the tan-dyed, compared with the other two finished fabrics, is due to the short fulling which it received; although this produced practically no area shrinkage, it decreased the bulk density of the fabric appreciably.

Mechanical Properties, General

In this study, the clearcut relations between the properties of the fabrics at various stages of manufacture and those of their constituent fibers which were observed in the worsted investigation are not evident. For example, dyeing weakens the fibers but strengthens the fabric, the extent of strengthening varying from one dye-lot to another. Clearly, minor changes in fabric structure due to incipient felting and similar factors perturb the fiber property–fabric property relationship. For this reason, most of the fabric property data are presented here simply as ratios of the values for the two wools, averaging over all the testing stations and conditions.

As the two wools did not diverge significantly from each other in their response to the various processes, either in terms of fiber or of fabric behavior, this technique yields a valid comparison of their performance.

TABLE V. Yarn Tensile Properties and Bulk Density

	High crimp	Low crimp	*P*
Modulus—g. grex^{-1}	9.45	10.80	0.001
Breaking tenacity—g. grex^{-1}	0.525	0.521	→1
Breaking extension—%	25.1	25.9	→1
Bulk density—g. cm.$^{-3}$ (at 120 g. cm.$^{-2}$ pressure)	0.185	0.193	→1

TABLE VI. Fabric Tensile Properties—Ratio High Crimp/Low Crimp

	Dry, 65% RH	*P*	Wet, pH 9.2	*P*
Initial stiffness	0.92	0.001	0.98	→1
Breaking load	0.95	0.001	1.00	1
Breaking extension	0.94	0.05	0.98	0.2

Fabric Tensile Properties

The relative values of three parameters derived from single-cycle tensile tests on 1-in. ravelled strips are reported in Table VI. They represent the aver-

TABLE VII. Fabric and Fiber Cycling Performance in Extension—Ratio High Crimp/Low Crimp

	Dry, 65% RH				Wet, pH 9.2			
	Fabric	*P*	Fiber	*P*	Fabric	*P*	Fiber	*P*
Woolen								
Set	0.95	0.1	0.99	→1	1.00	1	1.01	→1
Work loss	0.95	<0.001	0.99	0.2	1.00	1	1.01	0.2
Worsted								
Set	0.91	→0	1.00	1	1.00	1	1.00	1
Work loss	0.95	→0	0.99	→1	0.99	0.2	1.01	→1

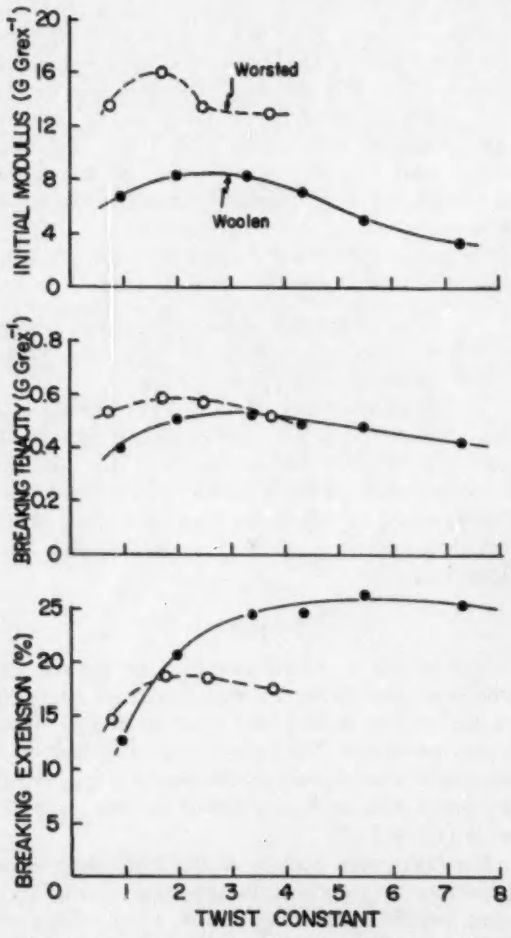

Fig. 1. Tensile properties of woolen and worsted yarns from the high-crimp wool as a function of twist. Twist constant = (turns/cm.)^2 × grex × 10^{-4}.

ages for the ready-to-dye and the three finished fabrics and for both fabric directions. These results are in broad agreement with those yielded by the worsted fabrics.

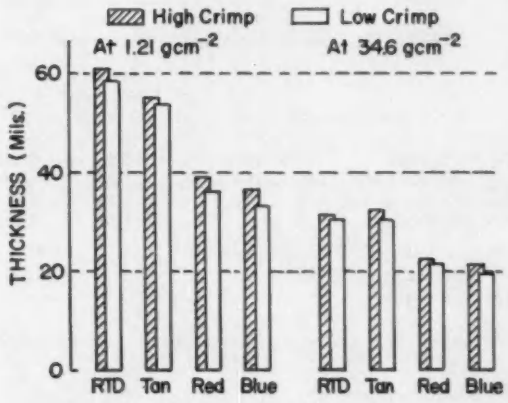

Fig. 2. Thickness of relaxed fabrics, on the second cycle of compression, at two pressures. *P* for wools: low pressure 0.05, high pressure → 0.

Bending Length and Flexural Rigidity

In Peirce's cantilever test, the bending length of the low-crimp fabrics was found, on the average, to be 4% greater, and the flexural rigidity 12% greater, than that of the high-crimp. These ratings agree precisely with those given by the worsted fabrics.

Cycling Performance in Extension

Cycling tests were performed both on the fabrics and on the fibers withdrawn from the fabrics. Half the breaking strain was selected as the cycling point, and the second cycle work loss and set were measured.[4] The ratios of the values for the two wools, for both the worsted and woolen series, are summarized in Table VII.

The data of the woolen experiment are in excellent agreement with those of the worsted; in both cases, the fabric recovery at 65% RH is markedly better for the high-crimp wool than the fiber performance would indicate; in neither case is there any difference between the two wools in the fiber recovery proper-

[4] See Figure 5 of Reference [2].

TABLE VIII. Fabric Laundering Area Shrinkage, %

	High crimp			Low crimp		
No. of launderings	1	7	10	1	7	10
Grey	18.3	23.9	25.0	17.9	24.7	26.2
Ready to dye	3.3	8.8	11.1	4.9	11.4	13.6
Finished—Tan	3.9	7.7	10.2	4.5	8.6	10.9
Red	4.1	8.2	10.4	4.6	9.2	11.4
Blue	3.7	8.1	11.0	4.5	9.5	12.5

P for wools <0.001; stages $\rightarrow 0$; times $\rightarrow 0$; W × S $\rightarrow 0.05$; W × T 0.1; S × T 0.01; W × S × T $\rightarrow 1$.

TABLE IX. Fabric Flex Abrasion Resistance

Test condition	Ratio high crimp/ low crimp	P
Dry (65% RH)	0.88	0.001
Dry (65% RH), solvent-extracted fabric	1.04	—
Wet (pH 9.2), severe test*	1.28	0.1
Wet (pH 9.2), mild test†	1.25	0.001

* Head load 1 lb., tension 2½ lb.
† Head load ½ lb., tension 1 lb.

ties, either dry or wet, or in the fabric recovery wet.[5]

Wrinkle Recovery

No significant difference in wrinkle recovery, measured at 65% RH by the vertical strip method, was observed between the fabrics from the two wools. (As in the worsted study, the recovery improved from the RTD to the finished state.)

Air Permeability

The results of measurements by the ASTM method (D737-46) are indicated by the bar graphs of Figure 3. The relative performance of the two wools, with the low-crimp fabrics being more permeable to air, is the reverse of that observed on the worsted materials.

Fulling Behavior

An experimental roller fulling mill was used to mill laboratory swatches, soap being the lubricant. All the test pieces were treated concurrently, and the length and width shrinkage was recorded at intervals. No significant difference between the two wools was found in the rate or ultimate extent of area shrinkage in any of the fabric states. (The RTD and the various dyeings did differ appreciably from each other.) Nor was any difference detected in a larger-scale test, where 10-yd. full width samples of fabric were fulled for 1 hr. in a standard size mill.

Laundering Shrinkage

Duplicate 12-in. square swatches of the grey, RTD, and finished fabrics were subjected to a series of mild launderings in a domestic washer, with an anionic detergent [1]. The samples were air-dried between washes. The dimensions were determined after 1, 7, and 10 launderings; the mean area shrinkage values for these times, based on the relaxed dimensions, are recorded in Table VIII. The low-crimp fabrics have a greater rate of laundering shrinkage, but the difference between the two wools is small.

Flex Abrasion Resistance

The ratios of the flex abrasion resistance (cycles to failure) values, obtained on the Stoll tester under various conditions, are given in Table IX.

The high-crimp fabrics have superior resistance to flex abrasion in the wet state, although there is no difference between the two wools in the ultimate tensile properties of fibers withdrawn from the fabric. Consequently, its superiority must be a fabric structure characteristic, presumably due to the crimp configuration.

Summary

Two Merino wools, differing in crimp content, but otherwise closely matched, were converted into yarn on the woolen system, and a ladies' weight dress fabric was made. The properties of the fibers and assemblies were evaluated; the results are in broad agreement with those of a similar worsted study already reported [2].

The fiber-crimp content of the high-crimp wool diminishes in yarn manufacture, that of the low-crimp remaining unchanged; both wools exhibit an increase in fiber crimp on going from yarn to ready-to-dye fabric. The high-crimp yarn has the lower initial stiffness in extension, but there is no detectable difference in yarn ultimate tensile properties or in yarn bulk density.

The high-crimp fabric is rated superior in softness and appearance by expert examination; it is thicker,

[5] The more detailed analysis possible in the worsted study does actually show that, even in the wet state, the fabric recovery for the high-crimp material is better than the fiber values indicate.

has slightly lower tensile properties at 65% RH, a lower flexural rigidity, and superior tensile recovery performance at 65% RH; the two wools are indistinguishable in fabric wrinkle recovery. The high-crimp structure has the lower air permeability (a reverse finding to that made on the worsted fabrics) and a lower shrinkage in laundering; it is inferior in resistance to flex abrasion at 65% RH, but superior wet (at pH 9.2).

Taken as a whole, the results show no greater an effect of fiber crimp in the woolen structure than in the previously studied worsted charmeen. This finding is contrary to expectation, which was that the more random and looser woolen structure would permit the fiber crimp to manifest itself more clearly.

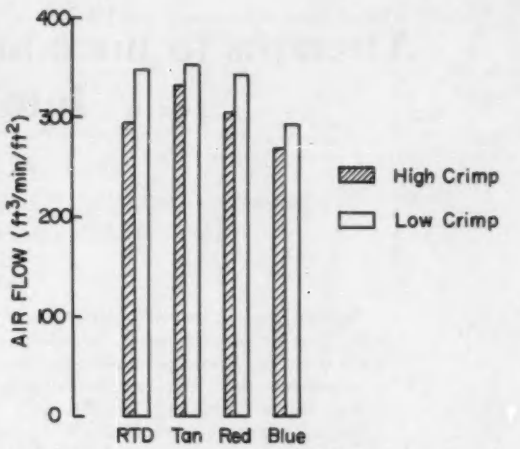

Fig. 3. Air permeability of relaxed fabrics. P for wools $\rightarrow 0$; for wools $\times$ stations $\rightarrow 0$.

Acknowledgments

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Attempts to Introduce Amide Cross-Links into Wool

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Abstract

Peptide-forming reagents have been applied to wool in an attempt to convert "salt links" into amide cross-links. Wool which has been modified with biscyclohexyl carbodi-imide is almost unchanged in weight, handle, and appearance but has increased resistance to attack by alkali, alkaline thioglycollate, urea-bisulfite, and trypsin. The mechanism of the changes involved is not known.

The extraction of wool with alkaline thioglycollate solutions has been developed as a routine test.

Introduction

It is widely supposed that "salt linkages" between acidic and basic side chains are an important structural feature of proteins [25]. Where such links occur between carboxyl groups (aspartic and glutamic acids) and primary amino groups (lysine), the possibility exists that these may be converted into covalent amide bonds, *viz.*

$$\left\{\text{—}CO_2^-\right. \quad {}^+NH_3\text{—}\left\{\right. \rightarrow \left\{\text{—}CONH\text{—}\right\} \quad + H_2O$$

Reactions of this type have been invoked to account for anomalies in the action of heat on horn keratin [18], collagen [15], and synthetic protein fibers [16], but so far there is little supporting evidence for this mechanism. It seemed possible that some of the reagents which have been developed for amide-bond synthesis in the peptide field might also convert salt links into amide cross-links. Such conversion would provide products which could be compared with the products of heat on the same proteins. If achieved in wool, this type of reaction would be expected to increase its resistance to damage during processing and in use.

The introduction of amide cross-links into gelatin has been achieved very recently by Sheehan and Hlavka [22], using a water-soluble carbodi-imide. Similar studies with wool using biscyclohexyl carbodi-imide and other reagents in an attempt to introduce cross-links have been carried out in this laboratory. Although there is no single criterion for detecting new cross-links in wool [2], reactions for example with difunctional reagents are known to exert in some cases a marked effect on fiber properties such as the alkali solubility, tensile strength, and felting characteristics. The formation of new amide cross-links should likewise decrease alkali solubility, since all the cross-links pre-existing in wool are alkali-labile. A decrease in the number of cationic side chains should also decrease the trypsin digestibility of the fiber. We have therefore used these two tests to follow the action of various peptide-synthesizing agents on wool.

Methods

The peptide-forming reagents which have been investigated include the following:

1. Tetraethyl pyrophosphite [3]
2. Phosphorus trichloride in pyridine [9]
3. Phosphorus oxychloride in triethylamine [26]
4. Biscyclohexyl carbodi-imide [20]

Since Reagents 1, 2, and 3 react instantaneously with water, they must be applied in an anhydrous solvent to dry wool. Reagent 4 reacts only slowly with water, hence can be applied in partly aqueous solution. The wool used was Merino 64's; the tips and root ends were removed and the greasy wool was scoured in petroleum ether (40–70° C.) and water. For the experiments under anhydrous conditions, the wool was dried *in vacuo* over phosphorus pentoxide for 2 days and then heated at 105° C. for 30 min.

Alkali solubility was determined according to the procedure of Harris and Smith [11].

Trypsin digestion was determined by pretreating 200-mg. samples of wool with pH 11 buffer (0.1 *M* caprate and 0.1 *M* piperidine) for 20 hr. at 30° C. and incubating with 5% trypsin in pH 8 buffer (0.1 *M* borate) for 4 hr. at 40° C. as described by Crewther [4]. The loss in weight was expressed as a percentage on a dry weight basis.

Alkaline thioglycollate solubility was determined by the method of Lennox (see Part II) under the conditions listed in Table I.

Results

The results of estimations of alkali solubility and trypsin digestion are given in Table I. There is a high correlation between the values obtained by these two methods in all the treated wools, which is remarkable considering the profound difference in their underlying mechanisms. Biscyclohexyl carbodi-imide is clearly the only reagent which modified the wool in the desired manner; that is, by increasing the resistance to alkali and to an even greater extent to trypsin. From Table I it is seen that the extent of modification was increased when partly aqueous solutions were used, presumably because swelling of the fiber enabled the reagent to penetrate more readily. All further work (Tables II and III) was therefore carried out using biscyclohexyl carbodi-imide, and wool treated with this reagent (2% in 80% dioxan, 3 days at 40° C., liquor/wool ratio 20/1) is hereafter referred to as "the modified wool." The modified wool is indistinguishable in handle and appearance from untreated wool. The solubility in alkali, alkaline thioglycollate solutions, and urea-bisulfite is markedly less than that of the controls (Table II). The modification process causes a weight increase of approximately 1%.

TABLE I. Resistance of Treated Wools to Alkali and to Trypsin

Treatment conditions			Alkali solubility, %	Trypsin digestion, %
Liquor–wool ratio 20–1 throughout	Time, days	Temp., °C.		
Controls				
Untreated	—	—	9.6	5
Pyridine	3	65	8.0	4
80% pyridine	3	40	8.5	4
Dioxan	3	65	9.1	4
80% dioxan	3	20	9.6	5
Biscyclohexyl carbodi-imide				
2% in pyridine	3	20	7.7	1
2% in pyridine	3	40	7.4	0
2% in 80% pyridine	3	20	6.8	−1
2% in 80% pyridine	3	40	5.7	0
2% in dioxan	3	20	7.5	−1
2% in dioxan	3	40	7.7	1
2% in 80% dioxan	3	20	6.2	—
2% in 80% dioxan	3	40	5.1	−1
Phosphorus trichloride				
0.5% in pyridine	3	20	11.2	11
0.5% in pyridine	0.5	65	14.9	12
0.5% in pyridine	3	65	19.7	18
2% in pyridine	3	20	9.3	9
2% in pyridine	0.5	65	10.7	7
2% in pyridine	3	65	19.6	23
Phosphorus oxychloride and triethylamine				
0.5% in pyridine	1	−15	11.3	
0.5% in pyridine	3	−15	10.9	
0.5% in pyridine	3	20	11.2	
0.5% in pyridine	3	50	11.4	
2% in pyridine	1	−15	11.7	
2% in pyridine	3	−15	11.4	
2% in pyridine	3	20	11.5	
Tetraethyl pyrophosphite				
2% in pyridine	0.5	65	10.8	7
5% in pyridine	3	20	9.0	6
5% in pyridine	0.5	65	11.2	5
5% in pyridine	3	65	13.1	20
5% in dioxan	3	20	8.7	4
5% in dioxan	3	65	8.8	5

Discussion

All the results of solubility tests suggest that the original aim to introduce new amide cross-links into wool has been achieved; however, other experiments (Table III) have yielded a less clear-cut picture. For example, load–extension measurements showed that the modification process caused no significant change in the 30% index and also no change in the decrease in work required for 30% extension when measured in 0.1 *N* HCl; this decrease may be considered as a measure of the salt links in wool [24]. Likewise the neutralization curves of untreated and modified wools, determined over the pH range 1.2–12.6 by the method of Da Silva, Stevens, and Whewell [5], were almost identical. On the other hand, the modification process caused a decrease of 0.4 moles of primary amino groups per 10^4 g. of wool (Table III). From this one may deduce that a very small number of new cross-links has been introduced. This may not be inconsistent with the solubility results, since in the reaction of formaldehyde and wool, McPhee [17] has shown that the intro-

TABLE II. Percentage Weight of Wool Dissolved by 0.1 *M* Thioglycollic Acid (100–1 Liquor–Wool Ratio, 1 Hr. at 50° C.) Before and After Treatment with Biscyclohexyl Carbodi-imide

	Adjusted to pH 11 with KOH			In 0.5 *M* K_2CO_3, pH 10.4		
	Dissolved initially, %	Removed by subsequent water washing, %	Total digestion, %	Dissolved initially, %	Removed by subsequent water washing, %	Total digestion, %
Untreated wool	4.5	54.5	59	14.7	16.9	31.6
Solvent treated wool	3.9	50.3	54	12.8	18.0	30.8
Modified wool	0.5	16.5	17	4.6	2.5	7.1

TABLE III

	Untreated wool	Solvent treated wool	Modified wool
Amide N content (% of total N)*	6.37	6.33	6.11
Primary amino groups (g. moles per 10^4 g. dry wool)†	2.1	2.0	1.7
Cystine content (g. moles per 10^4 g. dry wool)‡	4.83	4.85	4.76
Urea-bisulfite solubility (% dry wool)**	56.7	44.3	5.7

* Estimated by the method of Leach and Parkhill [12].
† Estimated by the method of Harding and McLean [10] as modified by McPhee [17] and Dr. C. M. Roxburgh of this laboratory.
‡ Estimated by the method of Shinohara [23].
** Estimated by the method of Lees and Elsworth [13].

duction of one new cross-link per 10^4 g. of wool markedly lowers the alkali solubility but does not affect the load–extension properties.

It is difficult to explain this marked stabilization of the wool protein in terms of other chemical interactions, since paper chromatograms of an acid hydrolysate of modified wool were qualitatively identical with those from unmodified wool, and the cystine content was quantitatively unchanged (Table III). It has been shown recently [8, 19] that biscyclohexyl carbodi-imide and similar reagents can cause dehydration of peptides containing asparagine and glutamine, presumably to form nitriles. Although the amide nitrogen content of wool was not altered by this modification process, this does not exclude the possibility that dehydration of these residues occurred during the process and that rehydration occurred under the conditions of amide nitrogen estimation. Carboxyl groups appear to be implicated in the modification process since the alkali solubility (11.9%) of esterified wool [1] was not decreased after treatment with biscyclohexyl carbodi-imide.

Unpublished work by Dr. J. M. Swan of this laboratory has shown that configurational changes in wool proteins cause a marked decrease in urea-bisulfite solubility. However, these structural changes also markedly increase the trypsin digestibility (Crewther [4]), and the observation that this treated wool is unattacked by trypsin makes it unlikely that configurational changes alone could account for the properties of the modified wool.

Physical adsorption of this reagent, or of biscyclohexyl urea, which is its reaction product with water, apparently does not account for the modification in view of the very small weight increase, which approximated only 1%. Solutions of this urea alone did not bring about any modification, and prolonged solvent extraction of the modified wool did not affect its properties.

It is intended to apply water-soluble carbodi-imides [21] to wool in future experiments; perhaps the results obtained using these reagents will remove the obscurities which have arisen during the present work.

Acknowledgments

The author is indebted to Dr. J. M. Swan for valuable advice, and to Miss E. M. J. Parkhill and Mr. L. M. Dowling for experimental assistance.

Part II: The Alkaline Thioglycollate Extraction Test for Wool

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FOLLOWING the use of alkaline thioglycollate solutions for the fractional extraction of wool proteins [6, 7] and for distinguishing between wools which have been subjected to various industrial treatments [14], the preparation of the reagent and its use have now been modified slightly to facilitate its application on a routine basis to wool samples.

The extractant is freshly prepared by diluting thioglycollic acid to a concentration slightly greater than 0.1 *M* with 0.5 *M* potassium carbonate (A.R.), titrating an aliquot with standard iodine solution, and adjusting the solution accurately to 0.1 *M* thioglycollate concentration; 20-ml. portions of this reagent are transferred to test tubes in a bath at 50 ± 0.1° C. and 0.2 g. of each of the wool samples to be tested is placed in each tube and stirred well to ensure rapid wetting. After 1 hr. at 50° C., the tube contents are filtered through folded Whatman No. 541 papers. Nitrogen may be estimated in aliquots of the filtrates by the semimicro Kjeldahl procedure and a factor of 6.25 used to convert percent nitrogen to percent wool protein. The weight of undigested wool may be determined by washing the residues repeatedly on the papers with water for 30 min. and drying to constant weight at 105° C. Samples (0.2 g.) of each of the wools are taken at the same time as the samples for extraction and dried overnight at 105° C. for estimation of the moisture content to permit expression of the percentage extraction on a dry weight basis.

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The Saturation Regain of Viscose Rayon Deduced from Density and Swelling Data

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Abstract

The moisture regain of viscose rayon in a saturated atmosphere has been estimated from measurements of the longitudinal swelling of the fiber at relative humidities ranging from dryness to saturation (water immersion). The density of viscose as a function of the regain has also been determined.

From these data, the volume swelling and the swelling of the cross-sectional area of the fiber have been calculated. The latter values, at the saturation regain deduced from the axial swelling measurements, are in substantial agreement with values which other investigators have determined by quite different methods of measurement.

Introduction

The relationship between the relative humidity and the moisture regain of viscose rayon has been studied by a number of investigators [4, 9, 22, 23, 25], but attempts to determine the regain of the fiber at saturation have produced values which show a wide discrepancy. The difficulty involved in any direct method of estimation lies in attaining a saturated atmosphere and at the same time preventing moisture from condensing on the surface of the fibers. The fact that a fall in temperature of 0.1° C. will increase the relative humidity of an atmosphere at 20° C. from 99.0% to 99.6% illustrates the difficulty and the degree of control involved in making measurements in the high humidity range.

Values for the saturation regain of viscose which have been published in the literature or which may be calculated from other observed physical properties of the fiber are not in agreement. Some lack of concordance can no doubt be attributed to differences in the type and history of the viscose rayon that was used in the experiments, but the discrepancies which are to be found in the data are greater than would be expected on this account alone.

A few attempts have been made by direct methods to determine the regain of viscose in a saturated atmosphere. Urquhart and Eckersall [23] measured the saturation regain by using a vacuum technique and were led to believe that the absorption and desorption curves for viscose rayon do not meet at saturation [12]. On the other hand, Ashpole [4] published results which were obtained by direct weighings at high relative humidities and concluded that in the case of viscose the hysteresis loop does close at saturation [3].

The experimental difficulties arising from moisture condensation in atmospheres approaching 100% relative humidity have led investigators to try indirect methods to estimate the saturation regain of textile fibers. Preston and Nimkar [19] determined the volume swelling by centrifuging moist viscose under standard conditions; as a check on the values thus obtained, the volume swelling was calculated from conductivity [16] and axial swelling [18] measurements. Cameron and Morton [5] reported the water retention of viscose after centrifuging wet fibers, and Preston and Chen [17] found the critical moisture content of the fiber, that is, the moisture regain in equilibrium with an atmosphere of 100% relative humidity [7], by using a rate of drying technique. A similar method was also used by Welo, Ziifle, and Loeb [24]. Preston and Bennett [20] determined the water content of the viscose at which migration ceases and suggested this as an indication of the saturation level.

It has been observed in the case of silk [8] and nylon [1] that there is a linear relationship between the volume swelling of the fiber and the moisture regain as saturation is approached. Indeed, it was also found that the relationship between the regain and the longitudinal swelling of these two fibers, except for the absorption at low relative humidities, can also be best described by a straight line. If the

same is true of viscose rayon, this provides a simple method of estimating the saturation regain of the fiber.

The present paper describes the results of experiments which were carried out some years ago as a preliminary stage of another investigation. The absorption and desorption isotherms for regular viscose rayon were determined at 21° C. The longitudinal swelling and the density of viscose at different moisture regains were also measured. The regain of the fiber at saturation was deduced from the axial swelling measurements and the volume and lateral swellings were computed from the experimental data as evidence in support of the estimated value for the saturation regain.

Experimental

The yarns used in all experiments were 300 den., 44 filaments, bright regular textile viscose manufactured by Courtaulds (Canada) Limited. Samples of the yarn as received from the spinning plant were prepared by extracting first with diethyl ether and then with ethyl alcohol. After all traces of alcohol were removed by rinsing in water, the yarn was soaked in distilled water for at least 24 hr. and then air-dried in a relaxed condition, at ordinary room temperature. Soaking in water and drying in a relaxed condition are important because internal strains which develop in the filaments during commercial processing must be removed before reproducible longitudinal swelling measurements can be made.

Moisture Regain

The moisture regain determinations were made by a procedure similar to that used by Abbott and Goodings [1] for nylon. Approximately 1-g. bundles of viscose filaments were suspended by means of a fine phosphor-bronze wire inside a stoppered weighing bottle which contained a sulfuric acid solution of the concentration needed to produce the required relative humidity [11]. The weighing bottle was placed inside a heavily lagged outer jar and the latter was immersed in a thermostatically controlled water bath which was operated at 21° ± 0.03° C.

The phosphor-bronze wire passed through a glass tube which was inserted into a hole in the rubber stopper of the weighing bottle. Thus it was possible to weigh the sample without removing it from the insulated jar; except for the few seconds required to make the weighing, the container was closed at all times by means of a small glass cap which fitted over the top of the opening. The samples were weighed at intervals of a day or more until the weight was constant to within ±0.0002 g.

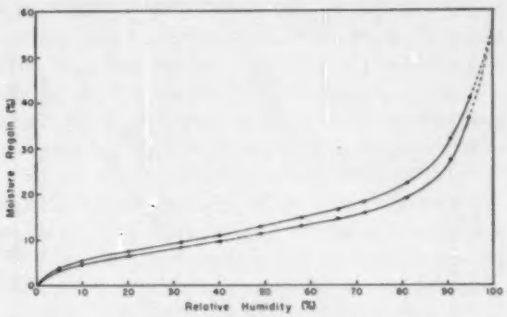

Fig. 1. Absorption and desorption isotherms of viscose rayon at 21° C.

TABLE I. Sorption Isotherms of Viscose Rayon at 21° C.

Relative humidity, %	Absorption regain	Desorption regain
5.1	3.2	3.8
10.2	4.5	5.3
20.3	6.4	7.5
31.8	8.4	9.7
40.2	9.6	11.0
49.3	11.4	12.9
58.3	13.0	14.9
66.2	14.7	16.7
71.9	15.9	18.4
81.1	19.1	22.3
90.7	27.4	32.0
94.8	36.4	41.1
98.1	48.0	—

At the beginning of the experiments, the samples were first dried to constant weight at 21° C. over anhydrous magnesium perchlorate. This required an exposure to the dry atmosphere of over six weeks. Moisture regains were determined under absorption and desorption conditions. The results are shown in Table I and have been plotted in Figure 1.

Longitudinal Swelling

Longitudinal swelling measurements were made at different relative humidities which ranged from dryness to saturation (water immersion). Single viscose filaments, approximately 85 cm. in length, were suspended in glass tubes through which air could be circulated in a closed system by means of a pump (Sigmamotor). The upper end of each filament was cemented to a stiff wire. Three small brass weights,

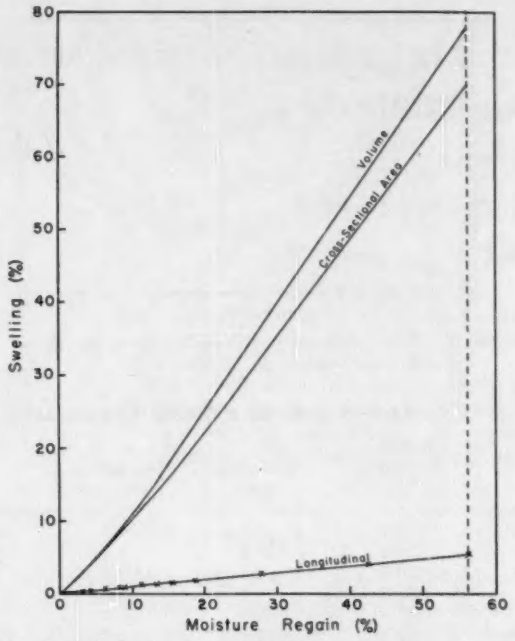

Fig. 2. Longitudinal, volume, and cross-sectional area swelling of viscose rayon as a function of the moisture regain.

TABLE II. Longitudinal Swelling of Viscose Rayon at 21° C.

Relative humidity, %	Longitudinal swelling, %
5.0	0.23
8.8	0.35
18.8	0.63
29.9	0.84
35.0	0.87
49.7	1.06
60.1	1.27
69.6	1.50
80.3	1.75
91.1	2.60
95.5	3.60
96.7	4.03
in water	5.27

weighing 0.05, 0.03, and 0.02 g. respectively and spaced about 1 cm. apart, were fastened to the lower end of the filament. By measuring the length of the filament successively under one, two and three weights, and plotting the results, an extrapolation could be made to obtain an estimate of the length under zero load.

While the filament was being conditioned, the weights rested on a wire gauze platform near the bottom of the tube. The top end of the tube was closed with a rubber stopper. A short length of

TABLE III. Density of Viscose Rayon at 21° C.

Regain	Density, g./cc.
0	1.515
4.0	1.517
6.2	1.514
8.8	1.507
11.4	1.500
13.2	1.490
14.3	1.487
18.0	1.472
25.5	1.436
40.0	1.374

2-mm. diameter glass tubing to which a short length of rubber tubing was attached passed through this rubber stopper. The wire from which the viscose filament was suspended projected through the rubber tubing, which could be closed by means of a pinchcock. Conditioned air entered at the bottom of each tube through a stopcock and passed out a side arm located near the top of the tube. Ten such tubes with a single filament in each were connected in series to a conditioning train made up of bubbling towers containing the required sulfuric acid solution, spray traps, and the Sigmamotor to recirculate the air.

The length of each filament was measured to the nearest 0.01 cm., and the longitudinal swelling was calculated as a percentage of the dry length. The experimental results are shown in Table II, and the relationship between the regain and the longitudinal swelling is plotted in Figure 2.

Density

The relationship between the density and the moisture regain of the viscose filaments was determined by a flotation method based on that described by Hermans [9] and modified by Abbott and Goodings [1]. Small samples of filaments cut to about 1-mm. lengths were conditioned in culture tubes by exposing them in a closed container to an atmosphere of the required relative humidity until equilibrium was reached. Each sample was then covered by quickly pouring a few milliliters of a nonpenetrating liquid of appropriate density into the tube. The contents of each culture tube were transferred to a 15-ml. centrifuge tube which was then filled with the same liquid. The liquids used were prepared by mixing benzene and perchloroethylene and their densities were determined with a pycnometer. All operations were carried out in a laboratory with the temperature controlled at 21° ± 1° C.

The tubes were centrifuged for 2 min. at a centrifugal acceleration at the outer end of the tube of approximately 2000 G. The maximum temperature rise which occurred during centrifuging was 0.8° C.; the temperature coefficient of the liquid mixture employed was 0.0015 g./cc./°C. The deceleration of the centrifuge produced currents in the liquid which tended to interfere with the settling of the filaments. To allow for this fact and to compensate for the effects of the slight rise in temperature, the tubes were placed in a water bath at 21° C. for 30 min. before a record was made of the position in the tube at which the filaments came to rest. The results obtained are given in Table III.

A procedure similar to that described by Hermans [9] was used to determine the apparent density in water. Small skeins of viscose yarn weighing approximately 0.5 g. were suspended by means of a fine platinum wire under distilled water. Air bubbles were removed by boiling the water for 10–15 min. at 40°–45° C. under reduced pressure. After the water was cooled to 21° C. and the yarn was allowed to remain under water for at least 24 hr., the skein was weighed while still immersed. The boiling, cooling, etc. were repeated until a weight constant to ±0.0002 g. was obtained. The apparent density in water of viscose rayon was found to be 1.618.

Discussion

Saturation Regain

The relationship between the moisture regain and the swelling of a fiber must be described by a straight line if the swelling is directly proportional to the volume of the uncompressed liquid water absorbed. If the fiber swells both longitudinally and laterally simultaneously, the longitudinal swelling can also be represented as a straight line function of the regain if the ratio between the longitudinal and the lateral swelling remains substantially constant.

In the case of viscose rayon, it was observed over the range of regains at which measurements were made that the relationship between the volume and the longitudinal swellings of the filaments could best be described by straight lines, except at low regains. Therefore, it is not unreasonable to assume that the longitudinal swelling plot can be extrapolated and will coincide at saturation with the point representing the axial swelling of the filament in water. This provides a simple and convenient way of estimating the saturation regain of the fiber. The longitudinal swelling in water was found to be 5.3%; from this, the regain of viscose rayon at saturation is estimated to be approximately 56%.

Some values for the saturation regain of viscose rayon which have been reported in the literature are given in Table IV.

The wide variation in the results shown in Table IV will be immediately apparent. It is known that repeated wetting and drying will alter the hygroscopicity of the fiber to some extent, and some differences can undoubtedly be attributed to the fact that measurements were made on different types of viscose. However, it is more reasonable to suppose that the accuracy of the data is also strongly influenced by the limitations of some of the methods of measurement that were used.

Preston and Nimkar [19] have pointed out that the centrifugal method for determining the amount of water imbibed by textile fibers is likely to yield results that are too high due to surface or "capillary" water which is not normally removed during centrifuging. In the case of viscose rayon, these authors

TABLE IV. Saturation Moisture Regain of Viscose Rayons

Saturation regain, %	Method used	Investigator
40–88*	Centrifugal method	Preston and Nimkar [19]
82	Centrifugal method	Ashpole [4]
90–100	Centrifugal method	Cameron and Morton [5]
76*	Centrifugal method	Carroll and Mason [6]
33–46	Vacuum method	Urquhart and Eckersall [23]
80	Direct weighing method	Ashpole [4]
38	Rate of drying method	Preston and Chen [17]
40 (approx.)	Rate of drying method	Welo, Ziifle, and Loeb [24]
40	High-frequency drying	Alexander and Meek [2]
40 ± 1	Migration method	Preston and Bennett [20]
58	Liquid permeability method	Carroll and Mason [6]

* Corrected for capillary water.

TABLE V. Swelling of Viscose Rayon at Saturation

Longitudinal swelling, %	Cross-sectional area swelling, %	Volume swelling, %
3.3–7.2 [18]	88–101 [15]	54–126‡ [19]
4.8 [10]	65† [14]	52–57 [24]
	66 [10]	68–136** [19]
	66 [24]	74 [10]
		82* [6]

† Swelling based on area of "conditioned," not area of dry fiber.
* Calculated from data given in reference cited.
‡ Determined by centrifugal method, corrected for capillary water and free space.
** Determined from conductivity and axial swelling measurements.

at first estimated the water held by surface forces to be of the order of 15% by weight and in later work [21] showed it to be closer to 25%. It would appear therefore that the saturation regains in Table IV which were determined by centrifuging wet fibers (except those marked with an *) should be reduced by about 25%.

Volume and Cross-Sectional Swelling

The percent volume swelling (S_r) at any regain (r) can be readily calculated from the density of the fiber at the same regain (D_r) and the density of the dry fiber (D_0).

$$S_r = \frac{D_0(100 + r)}{D_r} - 100 \qquad (1)$$

The relationship between the moisture regain and the percent cross-sectional area swelling (A_r) may then be calculated from the percent volume (S_r) and longitudinal (L_r) swellings.

$$A_r = \frac{100(S_r - L_r)}{100 + L_r} \qquad (2)$$

Values for the volume and the cross-sectional area swellings which have thus been derived from the experimental data are shown in Figure 2.

The longitudinal swelling of viscose in water was observed to be 5.3%. If the saturation regain is taken to be 56%, the volume swelling at saturation is approximately 78% and the swelling in cross-sectional area is approximately 69% (Figure 2). These results may be compared with other values which have been reported, from the summary shown in Table V. The number in brackets appearing after each value gives the literature reference.

The volume (V_a) to which 1 g. of dry fiber will swell at different moisture regains may be deduced from the results of density determinations. The relationship is illustrated by the solid curve in Figure 3. The broken line represents the calculated volume of the system composed of 1 g. of "dry" fiber of volume as determined in a penetrating medium such as water, plus the volume of absorbed water. As Hermans [9] has pointed out, the vertical distance between this line and the curve is a measure of the "free space" not yet filled with water. It should be noted that water which enters this free space does not cause the fiber to swell. The volume of free space found in the viscose rayon used in the present investigation is approximately 0.042 cc. (i.e., 0.660–0.618) or 6.4% of the volume of the dry fiber; this space becomes filled at about 25% regain. Available data give the volume of free space in viscose as approximately 6% of the volume of the dry fiber [13, 19].

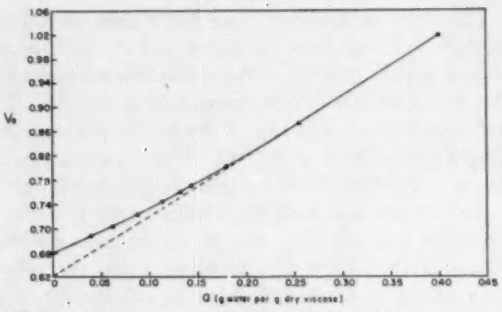

Fig. 3. Increase in the volume of 1 g. of dry viscose as a function of the moisture absorbed. Broken line represents the calculated additive volume of 1 g. viscose (measured in a penetrating liquid such as water) plus the volume of absorbed moisture.

Since the initial contraction in the total volume of the system when viscose fibers absorb water can be accounted for in terms of "free space" in the dry fiber, allowance should be made not only for the capillary water which is retained on the surface of the fibers but also for the volume of free space which absorbs water without swelling the fiber, if water imbibition values are used to estimate the volume swelling. This total correction appears to be of the order of 30% for viscose rayon.

Values for the volume of viscose in water which were obtained by the centrifugal and liquid permeability methods were reported by Carroll and Mason [6] in terms of the volume of swollen fiber in cubic centimeters per gram of dry fiber. The saturation regain values shown for these investigators in

Table IV have therefore been calculated by assuming that the specific volume of dry viscose is 0.66 cc./g. and the free space is 6% of the volume of the dry fiber.

These authors [6] measured the swelling of viscose in water by three different methods—vapor sorption and centrifugal and liquid permeability. Because of known limitations of the first two methods, and from the fact that volume determinations on fibers in a nonswelling medium gave results which were in accord with those obtained by direct measurement, these investigators concluded that the liquid permeability method gave correct values. The values for the saturation regain, the volume, and cross-sectional area swellings of viscose rayon reported by Carroll and Mason are in substantial agreement with those deduced by the author.

Summary

1. The moisture regain of bright regular viscose rayon has been determined at 21° C. under both absorption and desorption conditions for relative humidities which ranged from dryness to 98%.

2. The relationship between the longitudinal swelling of single filaments of viscose rayon and the amount of absorbed moisture has been determined for regains ranging from dryness to saturation (immersion in water).

3. The densities of viscose rayon in equilibrium with relative humidities ranging from zero to 96% have been measured by a flotation method. The apparent density in water has also been determined.

4. The volume swelling has been computed as a function of the regain from the results of the density determinations, and the swelling of the cross-sectional area of the fiber has been calculated from the volume and axial swellings.

5. The saturation regain of viscose rayon has been deduced from longitudinal swelling measurements and has been found to be 56%. This saturation regain is appreciably lower than other investigators have determined by vapor sorption or centrifugal methods, and it is higher than that observed by moisture migration or rate of drying techniques. The value is in substantial agreement with the saturation regain found for viscose by the liquid permeability method.

6. The volume swelling and the swelling of the cross-sectional area of the fiber based on 56% saturation regain are also in substantial agreement with values which other research workers have determined by quite different methods of measurement.

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A Study of Blended Woolen Structures

Part IV: Some Analytical Methods for Blend Determination

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Abstract

For statistical evaluation of blend variation along the length of strands, it is necessary to be able to determine the composition of a large number of small specimens. Microscopic techniques are useful, but tedious.

The present report describes two other methods which have been developed: densitometric and microanalytical spectrophotometric evaluation.

Introduction

With the development of statistical criteria [3, 5] useful for appraising the efficiency of blend distribution of staple strands, a demand has arisen for some precise, simple, and rapid analytical methods of determining blend composition of small specimens. The obvious procedure of counting fibers at cross sections which has been used by several workers [4, 8] can be rather tedious. In the case of a blend involving only color differences, rather than chemically different fiber types, the microscopic techniques may remain essentially the only reasonable method. This is also true of examination of distribution of fibers *within* cross sections.

For determination of average blend composition by weight in strands (sliver, rovings, yarns) or fabric containing different fiber types, a number of chemical methods may be used [10, 17]. The chemical methods almost always involve dissolution of one constituent of the mixture and recovery of the residue. The blend composition is then calculated from weight loss. Some of the methods require the use of arbitrary correction factors, depending on the partial solubility of the undissolved portion. In any event, the procedures are most conveniently used on specimens of relatively large weights if reasonable accuracy is to be achieved.

Large specimens may be useful for determination of average blend composition. To determine blend variability along the length of a strand, rather than average blend composition, it will generally be necessary to use a reasonably large number of rather small specimens. For example, specimens as short as a fraction of a fiber length (or at most as long as a few fiber lengths) may be taken, with the result that specimen weights may be in the order of a few milligrams.

It will be realized that the longer the specimen lengths from a given strand, the smaller will be the variation in blend composition from one specimen to the next. This poses a serious problem. When one attempts to employ larger specimen weights, convenient for normal gravimetric methods, he at the same time imposes greater stringency on the precision of his technique, if the errors in determination are not to mask the true variability of blend composition.

Two general analytical approaches have been developed to overcome this difficulty with reasonable success. One of these depends on specific gravity differences between the two fibers of a binary blend. The other is a spectrophotometric micro-analytical technique specifically for wool in wool–viscose mixtures but potentially adaptable for other fibers.

Densitometric Methods

The use of specific gravity measurements has been described as a means of identifying fibers, of identifying average blend composition where the fiber types are known, for the determination of resin pick-up or degree of crystallinity, and for following microstructural changes in fibers [1, 2, 7, 9, 11, 12, 13, 14]. The procedures in general require the use

of a density gradient column, although other adaptations have been used.

Titrimetry

It was hoped that a titrimetric method might be devised which would be simple, convenient, and sufficiently precise for the purpose of assessing blend irregularity. In principle the method would be as follows.

Two miscible fluids (e.g., CCl_4 and xylene) which provide a suitable range of specific gravities are used to prepare two standard solutions (A and B). These solutions are each adjusted to concentrations corresponding in specific gravity to one of the fibers. The stability of either solution can be therefore checked at any time by assuring that a sample of the appropriate fiber just floats in it.

An array of specimens is made simply by tying the strand into a large number of overhand knots and cutting these out of the strand. The length of yarn in a knot can be reasonably controlled by tying it under some constant tension and cutting it from the strand with a pair of razors mounted at a fixed separation on a steel plate.

A series of knots was prepared as follows. Four-inch lengths of yarn (3 Run woolen) were suspended from a clamp at one end, and a small weight (100 g.) attached to the lower end. The distance between the upper clamp and the point of attachment of the weight was measured. Then the lower end, with weight attached, was brought through a loop formed in the center of the length and allowed to drop, thereby making a simple overhand knot under the force due to the falling weight. The change in distance (ΔL) between the clamp and weight was found. The knot was then cut from the strand with the pair of blades mounted on a $\frac{1}{8}$-in. steel plate. The total length of yarn in the knot could then be calculated, as illustrated by the series of diagrams in Figure 1. The variability of length in such a series of knots is illustrated in Table I.

TABLE I. Average Length of Yarn in Knot and Variability

Yarn	Average length, in.	CV of length, %*
100% Wool	.250	6.0
25% Nylon	.266	5.9
50% Nylon	.260	4.9
75% Nylon	.267	5.2
100% Nylon	.246	5.5

* Twenty-five knots in each group.

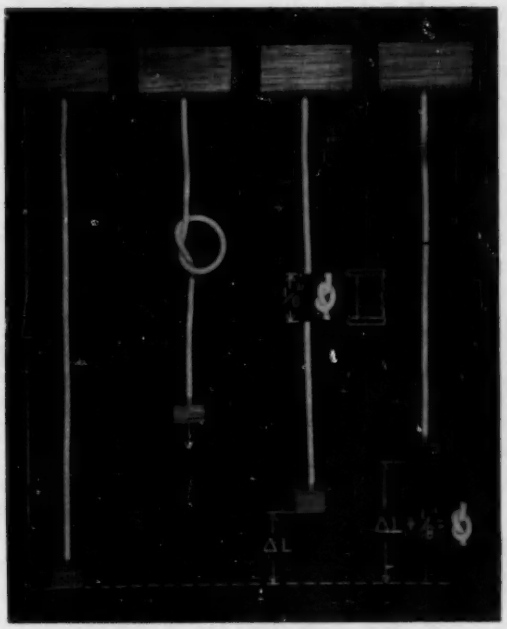

Fig. 1. Diagrammatic description of knot preparation and calculation of knot length.

An array of knots, say 25 at a time, is immersed in a small amount of standard mixture of the lower specific gravity. This is brought to the boil, then allowed to cool while the knots remain immersed. This step is intended to drive air and moisture out of the knots.

The average blend composition being known, a mixture of the two standard solutions is made up in a suitable proportion to allow all the knots to sink. The 25 knots are transferred with tweezers to this mixture in an erlenmeyer flask and allowed to settle down. Then standard solution of the higher specific gravity is introduced into the flask from a burette in measured amounts, raising the specific gravity of the mixture in steps. After each addition the knots and mixture are stirred and the knots then allowed to settle out. A count is kept of the number of knots floating at each level of mixture concentration. From this count, a curve of cumulative frequency vs. wool concentration may be drawn. Or, alternatively, a plot may be drawn on arithmetic probability paper from which the values of blend mean and blend standard deviation may be calculated.

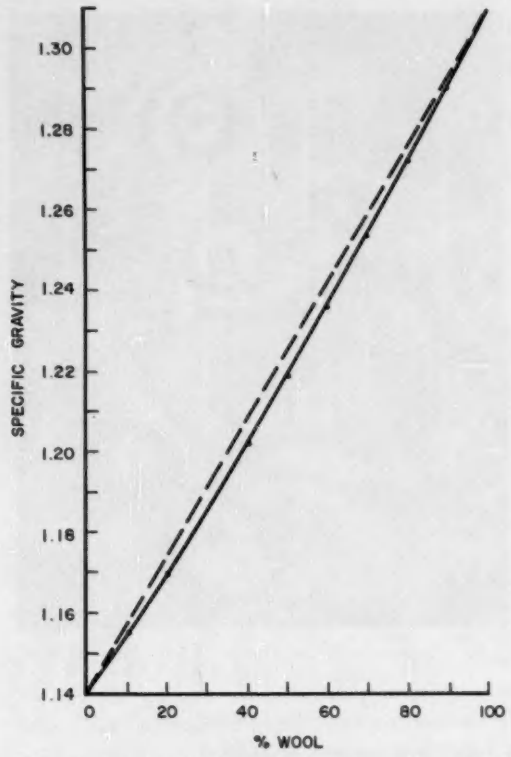

Fig. 2. Relationship between specific gravity and (a) curved line—percent wool by weight, (b) straight line—volume fraction of flotation mixture.

A word of caution is in order regarding the relationship of specific gravity and blend composition. One might at first assume that a 50:50 fiber blend would just float in a fluid mixture composed of equal volumes of the two fluids which each individually float one of the fibers in the blend. A little reflection on the problem will reveal that this is not true.

Fiber blending is done on a weight basis, whereas specific gravity will vary in a linear fashion with volume proportion. Thus, 50 cc. of a fluid of specific gravity 1.50, mixed (without volume change) with 50 cc. of fluid of specific gravity 1.30, will produce a specific gravity of 1.40. But this represents a weight proportion of $50 \times 1.50 : 50 \times 1.30$, or 75:65 rather than 50:50. To calculate the specific gravity corresponding to a given weight proportion of fibers,

$$(\text{specific gravity})_{\text{mixture}} = \frac{1}{\frac{\alpha}{(\text{sp. gr.})_\alpha} + \frac{\omega}{(\text{sp. gr.})_\omega}} \quad (1)$$

where $\alpha + \omega = 1$, ω = weight fraction of wool, α = weight fraction of other fiber, and $(\text{sp. gr.})_{\alpha,\omega}$ = respective specific gravities of the two fibers.

Figure 2 illustrates the effect just described. The straight line is the plot of specific gravity vs. volume concentration of the two standard solutions. The curved line is the plot developed according to Equation 1 for specific gravity vs. weight proportion of the two fibers. From these two plots it is simple to determine the volume proportion of a fluid mixture corresponding to a given fiber blend composition.

The titrimetric technique, on the face of it, seems very attractive from the point of view of ease. However, several factors interfere with the precision. In the first place, it can be shown that the change of specific gravity of a wool viscose mixture is only about 0.002 for a 1% difference in fiber blend composition. The thermal expansion of the organic solvents results in a change of about 0.001 in specific gravity per °C. The thermal expansion of the fiber is only about $\frac{1}{5}$–$\frac{1}{10}$ this amount. Therefore, to detect blend changes in the order 1–2% by this technique with an error of 0.1–0.2% requires temperature control to within ±0.2° C. This is by no means insurmountable in a constant temperature bath, but the use of such apparatus complicates the titration.

Another difficulty encountered with the use of CCl_4:xylene mixtures is the tendency for disproportionate evaporation of CCl_4. This could be overcome in the flask by keeping it capped, but is a serious problem when running the mixture out of the burette through the air. This, too, can be overcome by suitably introducing the titration mixture through a closed system.

There is a third problem resulting from variable moisture content of solvents and samples which reflects in variation of apparent fiber specific gravity. This could be overcome by keeping the liquids over silica gel and admitting air only through drying tubes, which of course raises additional technique problems.

A number of improvements in the method may be made; for example, CCl_4 may be replaced by a less volatile solvent, say, perchloroethylene. To avoid calculating solution concentration by volume measurements, the specific gravity can be directly checked during the titration. One way is by use of small beads of calibrated specific gravity kept in the flask with the knots. Another way would involve check-

TABLE II. Densitometric Determination of Blend Variability by Flotation Separation

Nominal 50% Wool : Nylon Yarn in CCl_4 : Xylene Mixtures

Mixture sp. gr.	Corresponding blend, % wool	No. of knots floating	Sample fraction floating
1.209	44	1*	.025
1.220	51	4	.20
1.222	52	8*	.20
1.227	55	8	.40
1.230	57	11	.55
1.231	57.5	10	.50
1.241	63	18	.90
1.270	79	20	1.00

* Forty knots used in these determinations; all others are samples of 20 knots.

ing the density of the mixture after each addition with a specific gravity balance accurate to the third place.

Flotation

In any event, the titrimetric methods leaves a great deal to be desired as a simple direct technique. However, its essential features may be preserved and its drawbacks overcome in the following procedure.

Having knowledge of the approximate average blend composition, the analyst makes up a solution of corresponding specific gravity. Similarly, several other solutions are made up, each known and differing from the mean concentration in some reasonably predetermined pattern. For example, one might calculate from theoretical CV of blend composition [5] the standard deviation of percent wool and make up solutions corresponding in density to the mean $\pm\frac{1}{2}$, 1, and 2 times the theoretical σ.

The several solutions are kept in convenient stoppered bottles or flasks and in a constant temperature bath. A relatively large array of knots is tied, cut, and boiled up in a solvent mixture of suitably low density to insure that they all sink. Then a separate group of knots (say 20) is dropped into each of the solutions of different specific gravity. After stirring the knots around in their respective flasks, making sure that they are separated from one another, allow them to settle at the constant temperature; the number of knots floating is counted.

From the number of knots floating at each specific gravity, an estimate of the population distribution of blend may be made. Table II gives some actual data found for a 50% wool:nylon blended woolen yarn. At least 20 different knots were submitted to the flotation analysis in each of 8 separate mixtures of carbon tetrachloride and xylene.

It can be shown that the data in the last column of Table II will yield a reasonably reliable approximation of the population blend distribution along the yarn. When this data is plotted on linear coordinates vs. the related blend composition (Column 2, Table II), a typical ogive (cumulative frequency distribution curve) results, as illustrated in Figure 3.

The same data may be plotted on arithmetic probability paper, as shown in Figure 4. If the population distribution is Gaussian or nearly so, a straight line of best fit may be drawn through the points, as has been done in the present instance. Indeed, for data of the sort under consideration, the straight line of Figure 4 is considered excellent.

While one could, by suitable manipulations, determine a population mean blend and an estimate of standard deviation of blend from Table II or Figure 3, the plot on probability paper (Figure 4) provides a most convenient graphical means of accomplishing the same results. The point where the line of best fit intercepts the ordinate 50 may be taken as a close approximation of the population mean, and where it intercepts ordinates 16.7 and 83.3 will be respectively minus and plus 1σ. Thus, Figure 4 immediately yields the values $M = 56.5\%$ wool, $\sigma = 5.75\%$ wool, from which the value of CV = 10.2% is computed.

To determine the excessive blend irregularity, the actual CV is to be compared with the theoretical minimum CV, as has been discussed in earlier parts of this series [3, 4, 5], which CV can be calculated from:

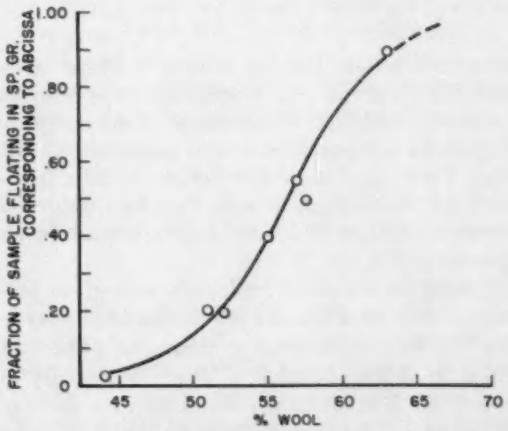

Fig. 3. Cumulative frequency distribution of blend determined by flotation.

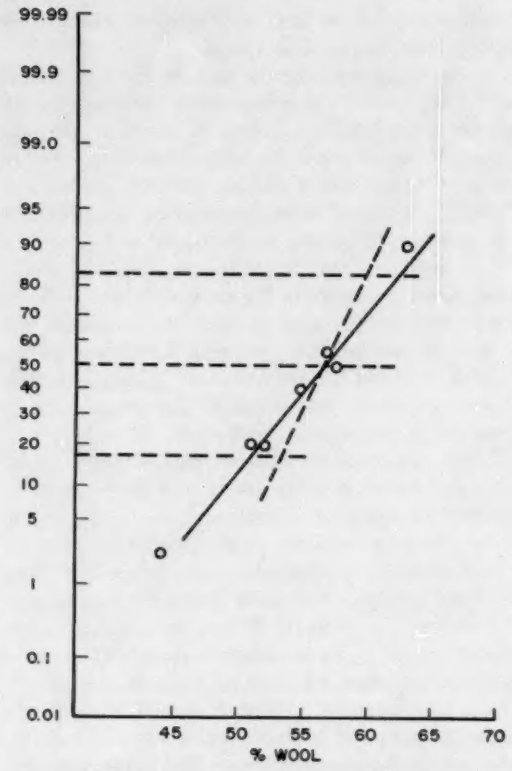

Fig. 4. Flotation data plotted on probability paper. (a) Solid line—best fit through experimental points; (b) dash line—theoretical random distribution.

$$\text{Ideal Random CV}_{\%\ \text{Wool}} = 100\sqrt{\frac{\alpha}{\omega}\frac{1}{\bar{D}}\left(\frac{\alpha d_w}{1 + L/l_w} + \frac{\omega d_a}{1 + L/l_a}\right)(1.05)} \quad (2)$$

where ω = weight fraction of wool in blend (presently 0.565), $\alpha = 1 - \omega$ = weight fraction of nylon (presently 0.435), $\bar{D}$ = average yarn denier (presently 900), L = specimen length (presently 0.26 in. from Table I), l_w, l_a = fiber staple lengths (presently 2.5 in. each), d_w = wool fiber average denier (presently 4.3), and d_a = nylon fiber average denier (presently 3.3).

Solution of Equation 2 using the data given produces a theoretical CV of 5.5% for the ideal random blend. The ratio of actual to theoretical (10.2:5.5) yields an estimated Index of Blend Irregularity of 1.85. This is excellent agreement with the value of 1.8 found previously for the same yarn by microscopic analysis of yarn cross sections and reported in Part II of this series. The dotted line of Figure 4 is drawn to correspond with the population distribution for the ideal random case.

Gradient Column

The gradient column method, while perhaps requiring somewhat more elegant apparatus and technique than the bottle flotation procedure, probably remains somewhat superior. A most convenient setup may be arranged in accordance with descriptions given in ASTM Standards Part 6 (1957 Supplement), ASTM Designation D1505-57T. The procedure follows closely one described by Tung [16] for preparation of a linear gradient. In addition, it employs calibrated glass beads distributed as primary density reference points in the column. (These beads are now available commercially from Scientific Glass Apparatus Co.)

Briefly, the method consists of first preparing a density column with carbon tetrachloride and xylene in a long measuring cylinder and submerging it in a constant temperature bath. The density range is chosen to provide a good separation among the knots eventually to be immersed in it. For example, the 50% wool:nylon blend would call for a spread from about 1.20 to about 1.28. Appropriate glass beads differing in specific gravity by 0.02 are then dropped into the column, and a plot of height in the column vs. specific gravity is prepared by sighting on the beads with a cathetometer (see Figure 5).

The yarn to be examined is cut into an array of knots, as previously described. The knots are boiled in solvent mixture and transferred to the column. They can be manipulated with a wire, to separate those which might become entangled, with surprising

TABLE III. Tabulated Values of Specific Gravity of an Array of Knots Distributed in Gradient Column

Specific gravity	Specific gravity	Specific gravity
1.2140	30	5
50	30	14
74	37	14
85	45	16
90	45	40
90	50	45
90	60	60
200	65	65
10	65	70
10	70	75
10	92	1.2435
20	300	1.2600

vigor before there is any notable disturbance of the gradient. An hour or so after introducing the knots into the column, sightings on each knot may be taken with the cathetometer, and a tabulation of the several specific gravities of the individual knots is prepared.

Table III gives a listing of specific gravities found for a typical array of 36 knots.

Although blend weight proportion and blend specific gravity have been shown to be related according to Equation 1, it is not necessary to convert each specific gravity to a corresponding wool percent in order to calculate the blend mean and standard deviation. This is true because, over the range of specific gravities encountered near 50% wool, the relationship between specific gravity and blend deviates insignificantly from linear. Thus the mean and standard deviations of specific gravity can be found first and then converted to percent wool. The data of Table III converts to values in good agreement with the determinations made by yarn sectioning and by the bottle flotation method (*viz.*, $M = 55.0\%$ wool, CV = 9.1%, approximate IBI 1.7).

Spectrophotometric Methods

Where preparation of a large array of knots is not feasible, as for example in slivers or low-twist rovings, the densitometric methods may prove unsuccessful. A micro-analytical procedure of some precision must therefore be adapted. One involving the near ultraviolet transmission characteristics of alkali-dissolved wool has been successfully developed for use with specimens of weights in the order of 2–5 mg. in admixture with viscose rayon.

The quantitative determination of colored materials by transmission intensity of their solutions is a familiar technique. Infrared and visible transmission spectra are, of course, widely used for both qualitative identification and quantitative analysis of pure compounds and molecular groups.

Recently in these laboratories [15] considerable attention has been directed to the use of the ultraviolet end of both transmission and reflectance spectra for analysis of so-called colorless solutions or solids. These frequently reveal specific absorption characteristics in the short wave-length region, conveniently analyzable on relatively common spectrophotometric instruments. In these laboratories the Beckman DU instrument, useful for analysis of spectra between 200 and 1500 mμ, has been employed.

The technique is relatively simple. The transmission of a known solution relative to that of the pure solvent is determined over a range of wave lengths. When plotted, there is often revealed characteristic absorption or transmission peaks for the solute (or solute:solvent complex). The intensity of peaks is expected to vary with concentration of solute in accordance with the Bouger-Beer Law.

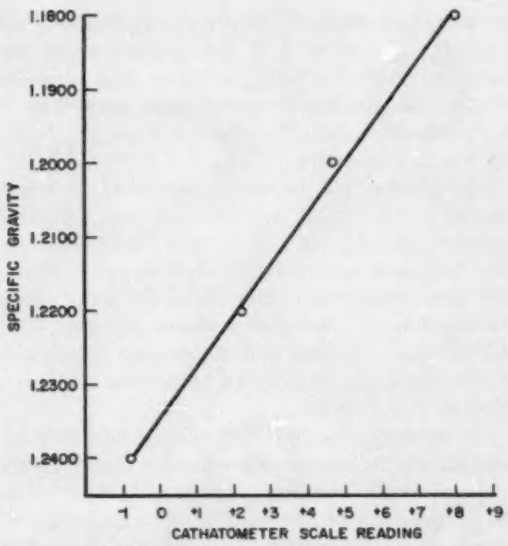

Fig. 5. Calibration of column with standard gravity beads.

$$\log_{10}\left(\frac{I_0}{I}\right) = c\beta = \log_{10}\left(\frac{1}{T}\right)$$

where I_0 = intensity of a given wave length passing through pure solvent; I = intensity of the same wave length passing through solution; β = empirical constant determined by cell, solution, and wave length; and c = solute concentration. For a particular wave length in a given cell and transmission system, the relationship reduces to

$$c = \log_{10}\left(\frac{1}{T}\right) \tag{3}$$

whence

$$\frac{c}{\mathrm{OD}} = K \tag{4}$$

where OD (optical density) = $\log_{10}(1/T)$.

A standard solution of known concentration is prepared and compared with pure solvent; the characteristic relative transmission spectrum is developed. A wave length corresponding to a given prominent peak in the spectrum is selected, and then the pro-

portionality constant K for that wave length is calculated. The value of K having been ascertained and checked over a range of known concentrations, solutions of unknown concentration may then be analyzed, employing the selected wave length and the empirically determined K.

The problem in hand was to determine the weight fraction concentration (conditioned basis) in small samples (ca. 2.5 mg.) of a wool:viscose mixture. The technique could employ either solvation of wool and spectrophotometric analysis of the wool:solvent combination or dissolution of viscose and analysis of this solution. In either case, the possible interference of the essentially undissolved component had to be eliminated or avoided.

An attempt to employ 70% sulfuric acid as a solvent for viscose was abandoned when erratic results were obtained. Optical density of the solutions varied quite out of line with known concentrations. It was also observed that gas bubbles evolved in time, suggesting progressive decomposition of the dissolved material. For what it is worth, one of the spectra obtained for a sample of viscose (without wool) dissolved in 70% H_2SO_4 is given in Figure 6.

One of the earlier attempts to take wool into solution for analysis employed 5% KOH, a concentration recommended by AATCC and ASTM for separation of wool from cellulosics. A typical spectrum for this solution is given in Figure 7, indicating a peak at 224 mμ. Repeat experiments with increasing concentrations of wool yielded the values of K at 224 mμ, as shown in Table IV. The variability was considered rather high, but at least a reasonable linearity between OD and concentration was observed.

In the course of further work, it was observed that the presence of viscose interfered with the determination of wool in 5% KOH. Some consideration was therefore given to the use of 1% KOH as a solvent for wool. This proved reasonably satisfactory, yielding the spectrum shown in Figure 8 (with a peak

TABLE IV. Concentration–Optical Density Relationship for Wool in 5% KOH at 224 mμ

mg. wool/ 50 cc.	Optical density	K*
0.5	0.147	3.40
1.0	0.241	4.13
1.5	0.352	4.26
2.0	0.487	4.11
2.5	0.590	4.23
3.0	0.708	4.23

* Wt. wool/OD.

TABLE V. Concentration–Optical Density Relationship for Wool in 1% KOH at 218 mμ

mg. wool/50 cc.	OD	K*
2.00	0.481	4.16
3.075	0.695	4.42
2.825	0.664	4.24

* Wt. wool/OD.

TABLE VI. Optical Density of Solutions of Viscose in 1% KOH at 218 mμ

mg. viscose treated with 50 cc. 1% KOH	OD of resulting solution
1.23	.039
2.23	.040
2.45	.046
3.55	.040
6.10	.040
9.98	.049

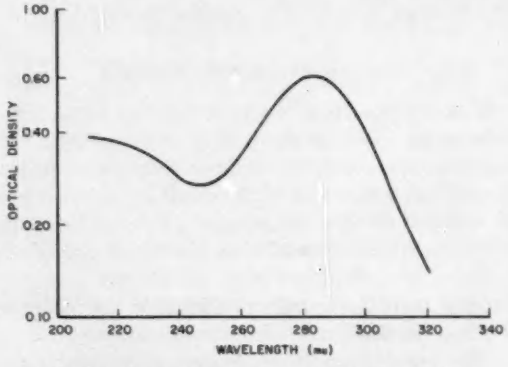

Fig. 6. Absorption spectrum of viscose in 70% sulfuric acid.

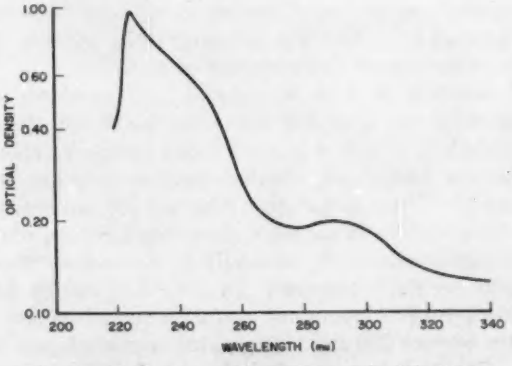

Fig. 7. Absorption spectrum of wool in 5% KOH.

TABLE VII. Effect of the Presence of Viscose on the Optical Densities of Solutions of Wool : Viscose Mixtures

Wt. wool, mg.	Wt. viscose, mg.	Optical density	OD − 0.042	Wt. wool / OD	Wt. wool / OD − 0.042
2.625	5.30	0.615	0.573	4.27	4.58
2.525	5.175	0.600	0.558	4.20	4.52
2.525	5.125	0.578	0.536	4.36	4.71
2.125	2.00	0.531	0.489	4.00	4.34
2.25	2.85	0.553	0.511	4.06	4.40
2.525	3.15	0.621	0.579	4.06	4.36
2.50	1.45	0.625	0.583	4.00	4.28
2.20	1.00	0.544	0.502	4.04	4.38

now at 218 mμ) and results for OD vs. concentration shown in Table V. The values are obviously quite similar to those obtained by use of 5% KOH, but again exhibit excessive variability for the analytical purposes in mind.

As for the possible interference of viscose, a series of tests were run in which various weights of viscose were boiled up in 1% KOH solution and a measure made of the resultant OD of these solutions at 218 mμ. The data are shown in Table VI, and it would appear that the solution reaches a saturation level with a rather low and reasonably constant value of OD, irrespective of the original weight of viscose.

A series of tests was then performed in which weighed amounts of wool and viscose were treated with 1% KOH. The values of OD vs. concentration of wool were calculated two ways. In one, no account was taken of the possible contribution of the viscose which may have resulted from its solubility. In the other, the arbitrary correction of 0.042, as derived from the data of Table VI, was made. The results are given in Table VII. It is obvious that these are still somewhat erratic and that the use of the correction factor for viscose does not add much to the consistency of results.

Some consideration was given to the various possible factors that might contribute to the erratic results. A comparison of the absorption curves of KOH and K_2CO_3 of equivalent concentration of potassium showed the carbonate to have a higher OD than the hydroxide. Absorption of variable amounts of carbon dioxide from the air on cooling the hot alkaline solutions seemed to be a likely source of difficulty.

Mild acidification of the KOH solutions after dissolution of the wool was therefore indicated, and proved to be the key to success of the technique. At the lower pH, however, there is a further shift in the transmission spectrum, as illustrated in Figure 8. The peak chosen for further studies was at 208mμ and the procedure was as follows.

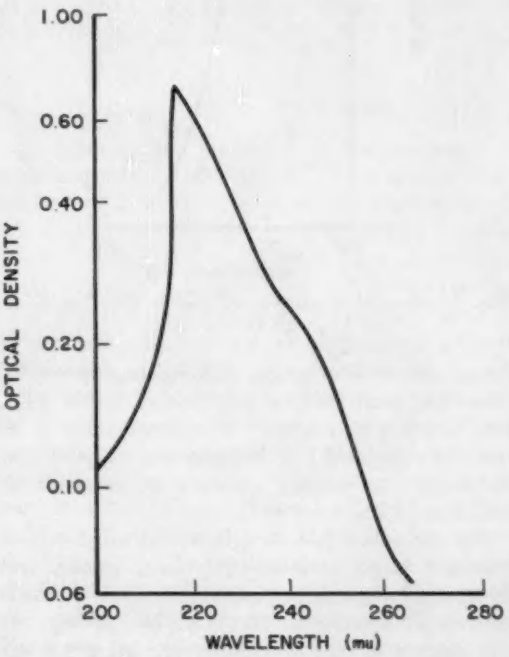

Fig. 8. Absorption spectrum of wool in 1% KOH.

1. Condition and weigh the sample of unknown blend composition on a milligram balance.

2. Treat the sample in 1% boiling KOH for 20 min., replacing evaporated water to make the volume up to the original level.

3. Dilute the solution with an equal volume of 4% solution H_2SO_4 and boil for 2 min.

4. Cool the resulting solution and measure its optical density relative to a control of boiled KOH: H_2SO_4, taking the OD value at 208 mμ.

The procedure was employed in the analysis of a number of preweighed series of samples of wool:

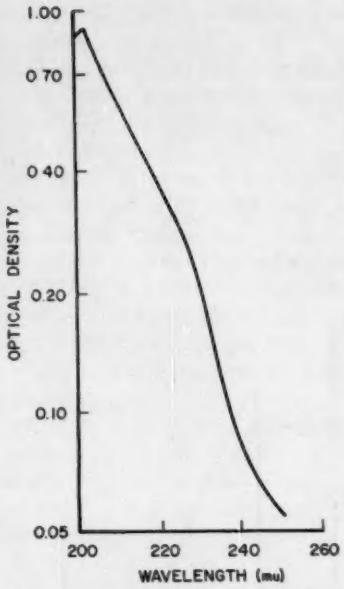

Fig. 9. Absorption spectrum of wool in KOH, acidified with H_2SO_4.

viscose and of wool alone, with satisfactory results. These are illustrated by the data of Table VIII, from which a satisfactorily consistent value of K could be calculated. It is interesting to note that the presence of viscose does not interfere under the conditions of test employed.

The procedure just described was employed to determine blend variability of yarn, roping, and sliver; results have been reported elsewhere (Textile Institute Conference on Blending, May 1958). It is of interest to note here, however, that there was excellent concordance between variability values determined by this micro-analytical method and by the tedious yarn cross-sectioning and fiber counting procedure.

Acknowledgment

The author wishes to credit Charles Lermond and Ruth Kenney for the development of the spectrophotometric technique described herein. Acknowledgment is also due Messrs. L. Barish and S. Golub for their efforts in the development of the densitometric techniques.

TABLE VIII. Optical Density Concentration Relationship at 208 mμ for Wool : Viscose Mixtures in KOH : H_2SO_4 Solvent

Weight wool, mg./50 cc.	Weight viscose, mg./50 cc.	Optical density	K*
1.690	1.584	0.691	2.446
1.792	1.102	0.733	2.445
1.924	4.054	0.788	2.442
1.760	—	0.721	2.441
2.058	—	0.844	2.438
2.296	—	0.931	2.466
1.684	—	0.690	2.441
1.862	—	0.764	2.437
2.100	—	0.857	2.450

* Wt. wool/OD.

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Fiber Damage in the Stock-Dyeing of Wool

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Abstract

The tenacity of wool is often reduced in stock-dyeing processes. As a result of this, many fibers are broken in the card. This reduction in tenacity has usually been ascribed to a damaging effect of the dye. However, our investigations show that most of the reduction in fiber strength is due to setting of bends or curvatures of the packed fibers by the hot water treatment. Such set fiber bends are nonuniformly strained by tensions and thus resist smaller loads than fibers set in the straight state.

Introduction

It is a common experience that stock-dyeing of wool, especially in dark colors [6], increases the brittleness of the fibers. There is a reduction of the fiber tenacity, which is usually ascribed to a damaging effect of the dye.

The effects on mechanical properties of fabrics and yarns by dyeing have been carefully investigated [3, 11, 13, 14, 15]. These experiments indicate little damage at common dyeing conditions. The effects on loose wool, however, are only little investigated. But there are observations that top dyeing can be made without appreciable damage in such cases where stock-dyeing under the same conditions causes large damage [8].

It is important to avoid fiber damage in stock-dyeing of wool, as such fibers have to pass through carding and combing, where they are subjected to high mechanical stress. If the fiber strength is low, a great many will be broken during these processes. Thus the mean fiber length of stock-dyed loose wool is sometimes reduced about 50% by carding.

Materials and Methods

Wool Material

Most experiments have been performed with a 64s soda-soap scoured Australian wool. Some experiments were done with a 64s dry-combed top.

Dyeing Method

The wool was dyed in a small laboratory dyeing apparatus with very good possibilities of controlling and varying the factors of interest: time, temperature, flow rate, pH, degree of packing, and concentration of the different dye bath components.

Testing Method

A simple method of measuring fiber strength is unfortunately not available. We have tried a fiber bundle test [1] and also laboratory carding combined with measurements of the mean fiber length. Neither of these methods was found to be quite satisfactory, as the degree of felting of the fibers influences the result too much. To evaluate the damage we had to determine the strength of single fibers, which demands a great number of measurements.

For the single fiber tests we used the Instron tensile strength meter. The fiber thickness was determined by a vibration method [10]. In mounting the fibers in the Instron apparatus and measuring their thickness, we used a load of 0.075 g. The crossbar velocity was 0.5 cm./min. and the sample length 1 cm. The measurements were made at 20° C. and 65% RH on fibers previously conditioned. The force and elongation at rupture were determined. The average strength of 75 fibers of the original wool was 1.33 g./den. and of the original top 1.20 g./den. Of the treated fibers, 25 were measured of each sample. The dispersion of the values was such that if the mean breaking strength of the treated fibers is 10% less than the mean breaking strength of the untreated fibers, there will be 95% probability of a real decrease. A diminishing of the breaking strength by 13% means 99% probability of a real decrease,

Results and Discussion

Our investigations confirm earlier results that loose wool but not top is damaged in dyeing. Further, we find from the load–elongation curves that the damage does not mean any change of the shape of the curve, but the breaking point is on the average

TABLE I

Treatment for 2 hr., 90° C., flow velocity = 1.3 l./min., degree of packing = 0.16 (cm.³ dry wool/cm.³ space)	Reduction of fiber tenacity, %		
	Loose wool	Top	Top fibers, randomly oriented
Dyed with a dark after-chrome dye	20.3	0.0	11.0
Acid bath pH 4–5	23.3	4.2	11.5
Water	24.8	8.3	12.5

TABLE II

Treatment in water for 2 hr., 90° C.	Reduction of fiber tenacity, %
Single loose wool fibers in flowing bath	10.5
Non-packed loose wool in stationary bath	10.5
Packed loose wool* in flowing bath	23.3
Packed loose wool* in stationary bath	23.3

* Degree of packing = 0.16 cm.³ dry wool/cm.³ space.

moved down the curve towards values of lower breaking elongations. This indicates that there is no important change in the overall fiber structure, but rather that the damage is concentrated to very localized parts of the fiber. This is also confirmed by the increased standard deviation for the breaking strength after dyeing. This deviation is about 0.22 g./den. for untreated fibers and rises to 0.30 g./den. for the damaged wool.

It might be suspected that the dye or some other dye bath component is responsible for the damage. However, a comparison between different bath compositions in Table I shows that a treatment with hot water alone is sufficient to cause damage.

Table I also indicates the large difference between loose wool and top for every type of treatment. This must be related either to the material itself or to the arrangement of the material in the dyeing vessel. The difference might be attributed to the following factors.

1. Loose wool contains some vegetable matter. Such impurities disappear together with short fibers during carding and combing. Further, some originally weak fibers are broken in these processes.

2. The fibers in top are quite straight and parallel, while loose wool fibers are bent and curled and oriented in a random manner.

3. Differences in orientation mean differences in fiber mobility under influence of liquid flow, which may give differences in mechanical strain of the fibers.

Experiments have shown that wool carded prior to dyeing behaves in the same way as regards damage as the uncarded, and therefore the first alternative can be excluded.

It is seen from Table II that the flow velocity has no effect on the damage. Thus it is not probable that the mobility of the fibers (third alternative) is of any importance. But from the same table it is seen that the degree of packing is important. Therefore the second alternative must be studied further.

If the fiber orientation has any effect, it should be possible to obtain a damaging effect after rearranging the fibers of the top in the same random way as in loose wool. After such a rearrangement we obtained the values in the third column, Table I, which show that such fibers are damaged, although to a smaller extent than loose wool fibers. This means that straightened fibers are considerably less damaged than curved ones. However, it is difficult to get top fibers back to the same state of random orientation as in loose wool. This probably explains the difference between the first and third column in Table I. If the degree of fiber bending and curling is decisive, loose wool fibers should not be damaged if they are kept straight during the treatment. This can be verified by experiments; if single fibers from loose wool are just straightened out and then treated in a hot bath in this form, there is no decrease in tenacity.

Nature of the Damage

Thus two conditions are necessary for this type of fiber damage: a hot water treatment must be applied and the fiber must be in a curved or curled state. Further, we know that the damage of the fiber is local.

Because of swelling we may possibly get such local tensions in the curved fibers in packed wool that the fibers will be damaged. We have not found any effect of this kind from microscopical investigations, and calculations show that the wet fibers, because of their extensibility, can take up large deformations of this kind.

The hot water treatment might cause a chemical degradation of the structure. But we cannot find any reason why a chemical damage should be eliminated or diminished by the low stress used to straighten the fibers. Moreover, it is not possible to prove any damage by chemical or microscopical tests.

However, hot water treatment may also mean a

chemical stabilization of the fiber structure by setting. We know that the intrinsic fiber properties are little influenced by setting, but the equilibrium state may be changed from a straight one to a curved one or the reverse [4]. Examining damaged loose wool in a microscope, we find that most fibers have sharp bends. These bends must have been set by the hot water treatment. When stretching such a fiber (Figure 1), the cross-sectional area at the bend will not be loaded uniformly. At a certain external load the inner part of the bend (the arrow) gets a higher tension than the outer one. The inner part is thus strained more and breaks earlier than the outer part. Thus the bent fiber will have a smaller breaking load than the straight one.

This has earlier been found by Barach and Rainard [2] by the addition of crimp to wool. To prove this effect of setting bends of the fiber, we performed the following experiment. Fibers from a sample, tested for damage by a hot water treatment, were straightened just to get the curvatures to disappear. They were now treated once more with hot water to get them re-set in the straightened form. The tenacity was measured and we found that the fibers had regained their original strength.

The magnitude of the radius of curvature of the bend is decisive for the extent of damage. Eeg-Olofsson [5], in examining fabric folds, has found that the decrease in fiber strength will be considerable when the fibers are set having a radius of curvature comparable to the fiber diameter.

Is it Possible to Avoid Damage by Setting?

We have found that the setting of sharp bends, present in packed loose wool, is the main cause of fiber damage in stock-dyeing wool. To avoid this we must either straighten the fibers or use such dyeing conditions that the damage will not appear.

A looser packing of the wool gives less bending of the fibers, thus probably smaller damage. Even in the non-packed state, however, loose wool may be damaged, but to a lower extent than in the packed state. But in this case there are differences between different wool qualities. The Australian wool used by us decreases 10% in tenacity when treated in a non-packed state (Table II), while a particular 64s Cape wool gets no damage under the same conditions. This means that in some wool qualities the fibers have sharp bends in the non-packed state too. Further, the damage of the Australian wool is independent of the degree of packing (cm.³ of wool per cm.³ of space) for degrees of packing higher than 0.045—a very loose packing. The damage on the Cape wool varies more with the degree of packing. However, to stand the packing produced by the flow itself, a packing degree of about 0.16 is necessary in practice, and this means severe (and the same) damage to both types of wool.

The damage is also influenced by the temperature, as the degree of set increases with the temperature. Figure 2 shows the decrease of fiber tenacity with increasing temperature after a water treatment for

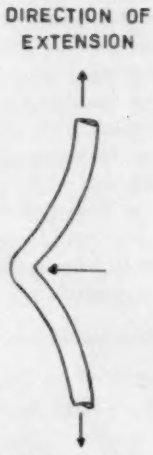

Fig. 1. Fiber with a set bend.

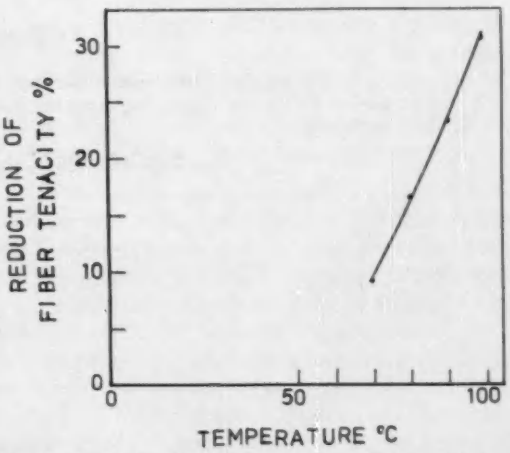

Fig. 2. Reduction of fiber tenacity as related to bath temperature after a treatment for 2 hr.

2 hr., which is comparable to conditions in practice. The damage is appreciable at about 70° C., and above that the fiber strength decreases rapidly with increasing temperature. Further, at 90° C. the difference between treatments for 1 and 2 hr. is insignificant. Here the wool is already damaged after a water treatment for 10–15 min. Dyeing at a low temperature or for a short time is thus desirable. Kärrholm [9] and Peters [12] have shown that dyeing is possible at these conditions if certain alcohols are added to the dye bath. Chrome dyes, however, cannot be used in this case, as chroming requires a high temperature or a long time.

Some dye assistants and also some dye bath components may have an additive effect in increasing or decreasing the mechanical properties of the fibers, either by acting upon the fiber structure or the degree of set. An experiment with the Australian wool with a cross-linking compound (sulfite lye [7]) did not show any effect, but certain dyeing conditions seem to decrease the degree of setting of the bends in particular wool qualities. However, no significant improvement seems to be possible without radically changing the dyeing procedure.

Acknowledgment

The author is grateful to Mr. B. Olofsson for valuable discussions of this work and for revising the paper, Mrs. E. Bernehed for performing the tenacity measurements, and Miss I. L. Carlström for help with some dyeing experiments.

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Manuscript received April 28, 1958.

Correction

In the article "Ultraviolet Absorbers" by R. A. Coleman and W. H. Peacock (September 1958), the fourth line from the bottom of the first column, page 785, should read as follows:

are improved 610%, the L1 dyeings are improved

Book Reviews

Research is People. Industrial Research Institute. New York, New York University Press, 1956. 69 + vi pages, illust. Price $4.00.

Reviewed by Howard J. White, Jr., Textile Research Institute, Princeton, N. J.

This book, which contains the proceedings of a meeting of the Industrial Research Institute, has the subtitle, "A Discussion of the Recruitment, Motivation, Recognition, Rating and Evaluation of Research Personnel." It is divided into three main sections entitled, "Recruiting Today," "Motivation of a Research Man," and "Rating and Evaluation of Personnel." The authors represent a cross section of people involved in research management and personnel training and include directors of research, college placement directors, and a variety of college professors.

As is usual with a symposium, there is a variety of styles and levels of presentation ranging from technical presentations to what might be called "after-dinner-speech" presentations. The technical level is higher in the third section than in the first two. On the average, the papers are well written, easy to read, and informative, if not particularly novel in ideas. This book can be recommended as pleasant constructive reading for anyone concerned with recruitment or management of technical personnel.

Man-Made Fibres. R. W. Moncrieff. New York, John Wiley & Sons, and Bungay, Suffolk, England, Richard Clay and Co., Ltd., 1957.

Reviewed by Richard E. Seaman, Pioneering Research Division, Textile Fibers Department, E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware

This work, which has run through two editions under the title "Artificial Fibres," now embarks on the third edition as "Man-Made Fibres." The author points out that this change in title has been made primarily because of the obsolescence of the term "artificial" as applied to synthetic fibers.

The format follows quite closely that of the earlier editions. The chief changes are inclusion of rather complete discussions of properties and behavior of the newer synthetics (as of 1957), as well as a considerably expanded list of fiber trademarks and manufacturers. Sufficient new material has been added to render older editions obsolete.

Being encyclopedic in nature, it follows that organization of pertinent material may be accomplished in several ways. The author has chosen to divide the book into three main categories: fiber structure and properties, discussions of specific fibers, and fiber processing. This has the advantage of allowing one to obtain, quite easily, information on a specific fiber, but necessitates repeating considerable basic information throughout succeeding sections. Notable in this respect is the treatment of dyeing and finishing techniques. One chapter is devoted to these subjects, but specific information must be obtained by reference to each fiber type. It is also unfortunate that, in view of their increasing importance, more space could not have been devoted to nonwoven fabrics and fiber blends as well as newer processing systems, such as the Perlock system and the Turbo-Stapler.

In general, however, the vast amount of up-to-date information regarding fibers that is contained in this volume should make it a welcome addition to any textile bookshelf.

Textile Chemicals and Auxiliaries. Henry C. Speel and E. W. K. Schwarz. New York, Reinhold Publishing Corporation, 1957. Price $13.50.

Reviewed by Hillary Robinette, Jr., Robinette Research Laboratories, Inc., Ardmore, Pa.

This second, completely revised edition of "Textile Chemicals and Auxiliaries," edited by consultants Speel and Schwarz, is a real improvement over the first edition. Through improved organization and the addition of new material, the volume has been expanded to 24 chapters. These chapters have been prepared by various well known specialists in the textile and textile chemical industries.

The book is divided into two parts; the first (containing eight chapters) deals with the physical and chemical aspects of fibers and fabrics and the physical-chemical aspects of the actual processing

of yarns and fabrics. All of the newer man-made fibers are mentioned and discussed. The second part consists of 16 chapters and covers the raw materials used in textile processing. Where possible, trade name products are identified. Adequate description of the technology of the application of dyes to the newer fibers is included. The techniques concerning the marriage of plastics and fabrics to form coated fabrics and nonwoven fabrics are adequately described.

Technical errors which appeared in the first edition, have been corrected or eliminated. The book is well written and is easy to read; each chapter has an excellent bibliography. The author index and the subject index are adequate.

This second edition of "Textile Chemicals and Auxiliaries" should prove useful as source material for courses in textile chemistry in textile schools and industrial chemistry courses at other institutions. Textile technologists, chemists, dyeing and finishing plants, and laboratory personnel of chemical manufacturers will find the book informative and a useful reference tool.

Emulsions: Theory and Practice. Paul Becher. New York, Reinhold Publishing Corporation, 1957. 392 pages. Price $12.50.

Reviewed by Hillary Robinette, Jr., Robinette Research Laboratories, Inc., Ardmore, Pa.

This volume, A. C. S. Monograph 135, is a lucid treatment of the knowledge available regarding emulsion theory and practices. In the first chapter Dr. Becher adequately defines his terms. The second and third chapters deal with the physical chemistry of emulsions. The fourth and fifth chapters discuss in detail the theory of emulsions from a physical-chemical standpoint. The sixth chapter discusses the chemistry of emulsifying agents. The seventh chapter is concerned with the mechanics of emulsification. The eighth chapter presents examples of emulsion applications. Chapter nine deals with the problems related to destroying emulsions or demulsification. Appendix A describes in detail testing procedures useful in the study of emulsion properties, and Appendix B is a compilation of the presently available commercial emulsifying agents listing composition, manufacture, trade name, and suggested applications. An adequate index is included.

This volume will prove extremely helpful to those working in the field of emulsion technology. Through careful study by those charged with the responsibility of applying emulsion technology to the development of commercial products, they may find their task made much easier.

The quality of the paper, the printing, and the binding is consistent with the high standards established for the A. C. S. Monographs.

"Emulsions: Theory and Practice" is recommended to all those having an interest in either the theoretical or practical aspects of the complicated borderline area of physics and chemistry surrounding emulsion technology.